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# SOAP FILMS

*A STUDY OF MOLECULAR INDIVIDUALITY*

BY

A. S. C. LAWRENCE

WITH A FOREWORD BY

SIR WILLIAM BRAGG, F.R.S.

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## FOREWORD

THE researches of the late Sir James Dewar on the properties of soap films are well known for their variety, beauty, and importance. For many years Mr Lawrence, who writes this little book, acted as Dewar's assistant. Being himself a good experimenter and a careful and interested observer, he acquired a remarkable knowledge of the technique of the researches; and while enthusiastically following the ideas of his master, he also tried to classify for himself the results that came to light.

A little while ago Mr Lawrence asked my opinion as to whether an attempt to put his practically acquired knowledge on record would be of any service. I encouraged his proposal warmly, for I was sure that such an account would contain a quantity of information and many considerations which would be of interest to the students of a subject now receiving so much attention. This book is the result. I hope and feel sure that there will be found in it ample reason why it should have been written.

W. H. BRAGG.

THE ROYAL INSTITUTION,  
*February 1929.*

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## INTRODUCTION

THERE is already a well-known book on this subject by Professor Boys; he calls his work "*Soap Bubbles and the Forces which mould them*," because he is mainly concerned with the action of surface tension as shown by soap bubbles.

In the following pages I have first described the origin and action of surface tension mainly to show that its direct action is confined to determining the form of films and bubbles. The large area of a soap film compared with the very small amount of liquid in it is quite at variance with our ideas of the form of liquids and the action of surface tension. Soap films do not exist as a result of surface tension, but in spite of it.

Our familiarity with soap films makes it necessary to draw attention to the fundamental problem which they provide. Why do they exist at all? We can only answer this by treating it as two separate questions; *what* is a soap film? and *how* does it manage to exist?

Recent discoveries in a number of different fields have been utilised to enable us to form a quite definite and convincing picture of the state of affairs in a soap film.

The subject forms a connecting link between several diverse lines of research which, however, all have the common factor of considering molecular individuality and its implications. There is no longer any need for regarding molecules and atoms as mere hypothetical units; that the properties of gases and liquids can be treated adequately as statistical means is the result of kinetic considerations. As soon as we come to deal with

surfaces these do not apply, because the molecules are anchored and we have to deal with a definite structure.

The individuality of an atom or molecule is the result of its form and the definite location therein of points or rather regions of chemical attraction. The degree of aggregation reached by a number of atoms or molecules, like or unlike, that is to say the structure of a mass of matter, depends on a number of factors, and is affected by spatial limitations. For example, it may go no further than the formation of a diatomic molecule as in the case of hydrogen; nevertheless, this active molecule still has residual forces of a specific nature, as shown by its absorption at the surface of palladium.

For these reasons, the chemistry of soap is dealt with rather fully, as also is the form and size of these molecules. Their behaviour when dissolved in water to form a soap solution is discussed in a later chapter. Meanwhile, a full account is given of the properties of soap films, especially of those discoveries made in the last few years. The variety of the metamorphoses of the soap film, described here fully for the first time, shows how many phenomena there are which must be included in any adequate theory of its nature and behaviour.

I have remarked on the way in which the soap film connects a number of diverse lines of research; equally interesting is the link which it provides with Thomas Young, one of Sir James Dewar's most distinguished predecessors at the Royal Institution, who has, incidentally, never received full credit for his work. His pioneer development of the wave theory of light has a direct bearing, of course, on the relation between thickness and colour of a thin film; he also first carried out the spectroscopic analysis of the light reflected from a soap film.

In 1805 he published a paper<sup>1</sup> on the cohesion of liquids which has undoubted priority over Laplace's later (independent) work; this latter is always treated as the classical theory of the liquid state, and Young was somewhat indignant that Laplace did not acknowledge his priority.

My own experience of the subject was gained at the Royal Institution when assisting in the latter part of Sir James Dewar's work on soap films. Where new facts or experiments are mentioned in the following pages, they are part of the enquiries made at the Royal Institution unless references to other workers are given. The microphotography of the stearolates and my repetition of Perrin's work on stratified films were also carried out at the Royal Institution at a later date by kind permission of Sir William Bragg. I should like to take this opportunity of thanking him for his interest in this work, and for the practical expression of it as permission to make use of the facilities of the Royal Institution.

Finally, I should like to thank Mr W. J. Green, assistant to the late Sir James Dewar and chemical assistant to the Royal Institution, for his numerous suggestions and constant interest in the preparation of this book and for the benefit of his unrivalled experience of the subject.

I am indebted to Professor J. W. McBain for several illustrations to which references are given in the text, and to the managers of the Royal Institution for the numerous photographs from the papers of Sir James Dewar published in the *Proceedings*.

<sup>1</sup> *Phil. Trans.*, **95**, 65 [1805].



# SOAP FILMS

## CHAPTER I

### SURFACE TENSION

MOST of us become acquainted with the soap bubble at an early age. Its form and ease of manufacture appeal to our nascent sense of workmanship. Subsequently, it is the amazing display of colour that impresses us most. Even when we have learnt to "explain" the colour formation as the result of an accidental relation between the wave-length of visible light and the thickness of the film, we can only wonder at our subjective consciousness of it.

In the past, scientific interest has been mainly concerned with the extraordinary tenuity reached by the thinnest films rather than with the significance of such thickness as they do possess.

The soap film is too often considered merely as a slab of soap solution in two dimensions only and, hence, as a dispensation of Providence for the demonstration of surface tension. The first part of this view is clearly incorrect, since a film must have some thickness, even if it be only that of a single molecule. The second part has led to the unfortunate conception of soap films as entirely surface-tension phenomena.

Every liquid has a surface tension; soap solutions are a small class of chemically and physically peculiar substances. It is necessary, therefore, to determine the exact rôle of surface tension before going any further. To do this we must consider the nature of surface tension generally.



We must remember that in a soap film one dimension is of the same order as those of its constituent molecules. We must, therefore, continually bear in mind the reality and behaviour of *individual* molecules.

### *The Origin of Surface Tension*

The classical theory of Laplace first <sup>1</sup> treated surface tension as a result of molecular attraction. In the simplest case, that of a gas, this attractive force shows itself in deviations from Boyle's Law at high pressures, where the molecules are brought into close contact. The corrected gas equation of Van der Waals

$$\left(P - \frac{a}{V^2}\right)(V - b) = rT$$

allows for this,  $a$  being the specific molecular attraction when the constant  $r$  is for 1 gram in place of the usual constant  $R$  which applies to the gram molecule.

In the case of liquids, this cohesive force causes two separate effects. As in a gas, the molecules are pulled together, the result being the same as if the substance were under compression by an external force. This equivalent compression is known as the "Intrinsic Pressure." <sup>2</sup>

The second effect is due to the existence of a definite surface. The molecules composing the surface layer are not acted upon by the same forces as those in the interior. Fig. 1 gives an ideal representation of the conditions: it is clear that there is an uncompensated pull acting on the surface layer inwards and normal to its plane. A similar effect will exist in the second layer and so on inwards, but the magnitude becomes negligible very quickly.

<sup>1</sup> See p. vii.

<sup>2</sup> T. W. Richards, *Chemical Reviews*, 2, 315 [1925].

The result of this inward pull is that the liquid tends to reduce its surface to a minimum. Individual molecules are sucked into the interior until the liquid assumes the form of minimum area, that is, the spherical form.

This effect causes the liquid to behave as if its surface were in a state of tension, and the force is therefore called "Surface Tension." It is clear from the argument that the intrinsic pressure is very much the larger force. Nevertheless, it is surface tension that is responsible for the characteristic form of liquids, while the intrinsic

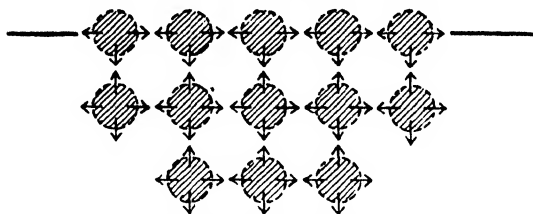


FIG. 1.—The origin of surface tension.

pressure is not in any way apparent, nor indeed can it be measured directly.

Tammann has shown that the substances which have the largest calculated intrinsic pressures are the least compressible, and that compressibility is inversely proportional to surface tension to a considerable extent.

The intrinsic pressure can be calculated from Van der Waals' equation.  $a$ , calculated from the critical constants of the vapour, is divided by the square of the specific volume. This method gives for water the surprisingly large value of 11,000 atmospheres; alcohol and ether being 2400 and 1400 respectively.<sup>1</sup>

<sup>1</sup> Walden has shown the intrinsic pressure is equal to 75 times the surface tension at the boiling-point, and also that the critical pressure is 2.22 times the surface tension at the boiling-point. The intrinsic pressure can also be calculated from the latent heat of vaporisation. By this method it is found to be 10,500 atmospheres for water.

Surface tension is much more readily appreciated and measured. Its action, especially in soap films, is best illustrated by Maxwell's diagram (Fig. 2).  $ABCD$  is a

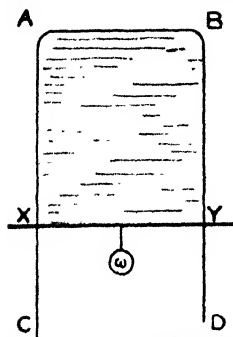


FIG. 2.—Maxwell's surface tension diagram.

vertical wire frame over which the wire  $XY$  slides without friction, enclosing a film  $ABYX$ . To  $XY$  is attached weight sufficient to prevent movement upwards under the influence of surface tension or downwards under gravity.  $XY$  is now pulled down by an additional force, so that the area of the film and, correspondingly, its free<sup>1</sup> surface energy is in-

creased. The increase of free surface energy is equal to the product of the increase of area and the surface tension. Surface tension may, therefore, be defined as the free surface energy per unit area which is equal to the work required to form unit area.

It should be observed that the work required to increase the area of  $ABYX$  by a given amount is independent of the area of the film. In this respect surface tension differs from elasticity, with which it is frequently compared and confused.

Of course, a plane film can only contract in its own plane, but it must be remembered that surface tension is acting normally to that plane.

### *Measurement of Surface Tension*

It has been pointed out that a mass of liquid, under the influence of surface tension, strives to take up a

<sup>1</sup> The increase of surface is accompanied by absorption of heat. The total surface energy is therefore greater than the free surface energy by this amount.



PLATE I.

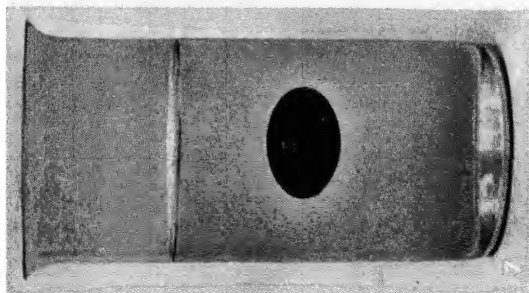
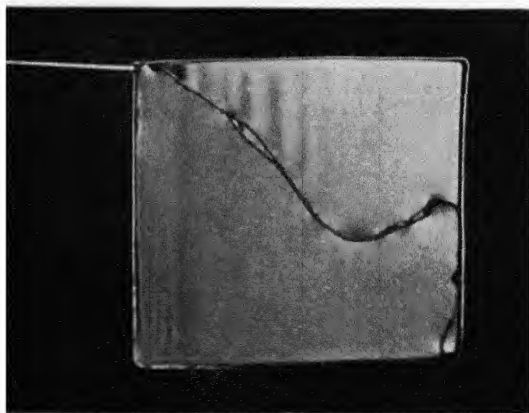
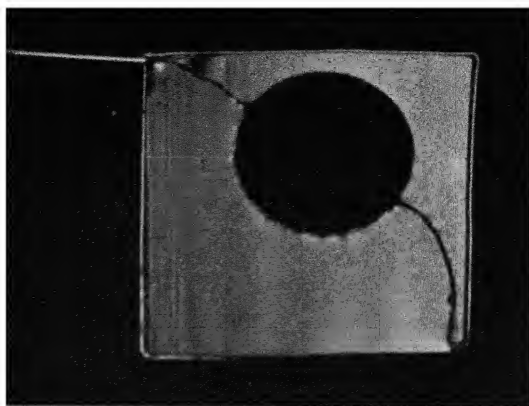


FIG. 3.—“Drop” of ortho-toluidine suspended in brine.



(A)



(B)

FIG. 12.—The action of surface tension in a soap film.

spherical form. That it only partially succeeds is due to the distortion caused by its own weight. Very small drops of a substance, such as mercury which has a large surface tension, are practically spherical. This distortion may be eliminated by suspending the liquid in another of equal density. Fig. 3, Plate I, shows a "drop" of ortho-toluidine weighing some 40 gm. suspended in brine.

Usually, drops are supported from above, as in the familiar case of a liquid dripping from a tube. At the moment of separation of the drop from the nozzle, the downward pull of gravity is just overcoming the upward force of surface tension acting around the "neck" of separation. Several methods of determining surface tension <sup>1</sup> have been worked out on this principle.

In contradistinction to liquid drops in air are gaseous bubbles in a liquid. Here, again, the effect of surface tension is to reduce the free surface energy, with the result that the gas in the bubble is compressed. If we consider a plane through a spherical bubble in a liquid of surface tension  $\sigma$ ; then, if  $D$  is the diameter of the bubble and  $p$  the compression,

$$\pi D\sigma = \frac{\pi D^2}{4}p,$$

so that

$$\sigma = \frac{pD}{4} \quad . \quad . \quad . \quad (1)$$

Any gaseous bubbles in a liquid, therefore, are under an excess pressure which is inversely proportional to their diameter. If this is very small,  $p$  may become large. We actually have this state of affairs in a liquid at its boiling-point. For the formation of the first microscopic bubbles of vapour the temperature of the liquid must be

<sup>1</sup> For a full account of methods of measuring  $\sigma$ , see Freundlich, *Colloid and Capillary Chemistry*, English trans., p. 16 *et seq.*

raised well above the boiling-point under atmospheric pressure, since the bubbles are being expanded by vapour boiled off under considerable pressure. When the bubble begins to expand, the internal pressure falls rapidly and the bubble bursts violently, so causing "bumping."

Theoretically, a pure liquid would never boil. The formation of the first infinitely small bubble of vapour which would be under enormous pressure would require an impossibly high temperature; long before this was reached the liquid would pass freely into vapour at its surface without ebullition. Ordinarily, liquids when raised to their boiling-point give off their dissolved air in small bubbles. In accordance with Dalton's Law of Partial Pressures, the liquid exerts its normal vapour pressure, corresponding to the temperature, inside the air bubbles; these rise to the surface, and so promote steady ebullition. A porous chip is used in distillation to provide a steady stream of small air bubbles. The bubbles of air must not be too large, else they rise to the surface before the liquid has exerted its full partial pressure. This is the cause of the comparative inefficiency of the capillary tube as used in vacuum distillations to provide a stream of air bubbles. The liquid requires to be superheated considerably.

The soap bubble differs from the bubbles just described in that it has two liquid/air interfaces instead of only one.

If we consider a plane through the centre as before, we have for the condition for equilibrium:—

$$2\pi D\sigma = \frac{\pi D^2}{4}p,$$

so that

$$\sigma = \frac{pD}{8} \quad . \quad . \quad . \quad (2)$$

This does not provide an accurate method for the measurement of surface tension owing to the smallness of the pressures involved. The internal excess pressure of a bubble 10 cm. in diameter is of the order of 0.2 mm. of water.

A more satisfactory method of determining the surface tension of a liquid is by observation of the height to which it rises in a capillary tube. Liquids which wet glass rise in a tube immersed in them to a height above the surface which depends on the diameter of the tube and the surface tension of the liquid. This occurs because the liquid creeps up the walls of the tube, wetting them and so increasing its surface; this is reduced by the rise of the liquid in the tube. It therefore continues to rise until the mass of the column of liquid just balances the upward pull of surface tension acting round its circumference. Using the same symbols and if  $\Delta$  is the density of the liquid,  $g$  the acceleration due to gravity, and  $h$  the capillary elevation, then

$$\pi D\sigma = \frac{\pi D^2 h \Delta g}{4},$$

so that

$$\sigma = \frac{D h \Delta g}{4} \quad . \quad . \quad . \quad (3)$$

This method requires complete wetting of the glass tube by the liquid used. It has recently been shown<sup>1</sup> that this is the case for water; a point upon which some doubt formerly existed. The angle of contact is, in fact, zero.

Liquids not wetting glass are depressed below the surface of the liquid, the argument being similar in every other respect to the first case.

Tubes whose diameter is small enough (c. .25 mm.) to cause a capillary elevation of a few centimetres are

<sup>1</sup> Richards and Carver, *Journ. Amer. Chem. Soc.*, **43**, 827 [1921].



difficult to clean, and so a fresh tube is sometimes used for each determination. A piece of glass tube is drawn out in the blowpipe and suitable lengths cut off for use. The height to which the liquid rises is measured in the usual way; the top of the column is also marked. The tube is then cut in half at this point and the diameter measured microscopically. As long as the diameter is known at the point where the surface tension is acting, the tube need not be uniform. Ellipticity must be guarded against.

One more method must be mentioned. A wire ring in the plane of the surface of the liquid is attached to one arm of a balance, and the pull due to surface tension directly measured.

The numerical values of the surface tension of various liquids vary from a few dynes/cm. for the liquefied gases to several thousand for molten metals. That of water is 73 at 18° C. Most organic liquids have values of about one-third of this. Surface tension varies with temperature, becoming zero, of course, at the critical point.

### *The Surface Tension of Solutions*

The surface tension of a solution is more complicated. If we are to consider individual molecules we cannot regard solutions as homogeneous, and so we have another factor to consider.

It is found that, in general, inorganic substances raise the surface tension of water while organic lower it.

Soap solutions are remarkable for the very large reduction brought about by quite small concentrations of soap. Fig. 4, which gives the results of several workers <sup>1</sup>

<sup>1</sup> Lascaray, *loc. cit.*, p. 16; Harkins and Brown, *Journ. Amer. Chem. Soc.*, **39**, 361 [1917]; Walker, *loc. cit.*, p. 16; Narayan and Subrahmanyam, *Phil. Mag.*, **43**, 663 [1922]; Sir J. Dewar, *loc. cit.*, p. 22.

for solutions of sodium oleate in water, shows the typical form of curve connecting surface tension and concentration of soap solutions. It will be seen that the curves show marked divergences at low concentrations, but that they agree for more concentrated solutions.

It is customary to regard the surface tension of a liquid as one of its physical constants. This is most undesirable in the case of solutions. We do not measure

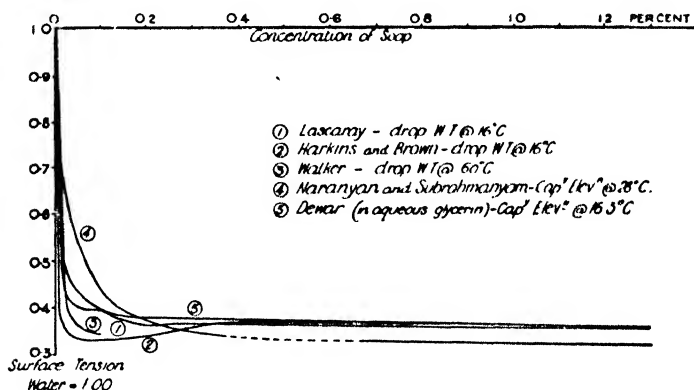


FIG. 4.—Surface tension of sodium oleate solutions.

the surface tension of the solution in bulk but the tension of the surface of the solution. We have no right to assume that this surface in any way reproduces the constitution of the bulk of the liquid.

Measurements of the surface tension of solutions whose surfaces are continuously renewed throw light upon this point. The values obtained in this way are known as "dynamic" surface tensions in contradistinction to those obtained by the methods outlined above, which are called "static." For soap solutions the results are very remarkable.<sup>1</sup>

<sup>1</sup> Lord Rayleigh, *Proc. Roy. Soc.*, **47**, 281 [1890].

These results can have only one meaning, namely, that we are measuring the tensions of different surfaces,

Per cent. soap.	Surface Tension.	
	Dynamic.	Static.
0.025	77 dynes/cm.	53 dynes/cm.
0.25	77 " "	25 " "
1.25	60 " "	25 " "
2.50	56 " "	25 " "

and that the low value of the static surface tension is due to the formation of a specific surface layer which takes a definite time to form and which is most persistent in more concentrated solutions.

Pure liquids establish their static surface tension in less than 0.001 second. An aqueous solution of amyl alcohol took more than 0.02 second.

These results are confirmed by the remarkable work of de Noüy<sup>1</sup> on soap solutions at extreme dilution. He found that sodium oleate at a concentration of  $10^{-5}$  affects the surface tension of water but slightly at first. On standing, however, for 2 hours, a drop of more than 25 dynes ensues; one-millionth part of soap does not lower the surface tension of water at all initially, but after standing for 2 hours brings about a drop of 20 dynes.

To sum up, we may say that soap solutions possess a specific surface layer which takes a definite time to form, and which is responsible for the smallness of their surface tension.

<sup>1</sup> *Phil. Mag.*, **48**, 264, 664 [1924].

The formation of a layer possessing properties different from those of the solution in bulk is not, however, confined to soap solutions. Saponin solutions have a surface viscosity sixty times that of the solution in bulk. Aqueous solutions of certain dyes, such as fuchsin, form solid skins under conditions which preclude evaporation; they are not formed at the surface of the alcoholic solution. Correlated with these surface layers formed from solution are those formed in other ways.

The attraction of a layer of gas to the surface of mercury lowers its surface tension considerably. Tungsten, even at white heat, collects a "skin" of oxygen sufficient to reduce the emission of electrons largely. Langmuir <sup>1</sup> has shown that this is a monomolecular layer of oxygen and not of oxide.

These very thin layers are further exemplified by the spreading of fatty substances on water. These latter must obviously be closely compared with the hypothetical layer which we have assumed to exist at the surface of soap solutions.

The structure and dimensions of these layers will be discussed in a later chapter. Meanwhile the conception of a specific surface layer leads to certain *a priori* possibilities.

The simplest surface layer is monomolecular. Such layers are only known on the surface of water,<sup>2</sup> and are only formed of long-chain molecules which contain an active group at one end, this activity consisting of a powerful affinity for water. The layer should therefore be regarded as a double layer, one-half of which is fatty substance and the other water. The corresponding stable film would be a sandwich structure consisting of

<sup>1</sup> *Journ. Amer. Chem. Soc.*, **38**, 2271 [1916].

<sup>2</sup> Or other liquids, such as mercury or calcium-chloride solution.

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<sup>1</sup> *Journ. Amer. Chem. Soc.*, **38**, 2271 [1916].

<sup>2</sup> Or other liquids, such as mercury or calcium-chloride solution.

a sheet of water covered at its two surfaces by monomolecular layers of fatty substance.

As we shall see later, the soap film has a structure of this sort. It has been suggested that the thinnest possible soap film is one which has lost all the internal liquid and thus consists of a bimolecular layer of the fatty acid. This is the form of the solid substance, but entirely fails to explain the behaviour of soap films.

## CHAPTER II

### SOAP

Most of the investigations of the properties of soap films have been carried out with impure materials. The published directions for making up soap solutions are reminiscent of Mrs Beeton.

Soap is not—just soap. In fact, it is not easy to define either soap or a soap solution; nor is the connection between them as simple as might be imagined.

The name “soap” means little more than the potential property of forming a soap solution when dissolved in water. Such properties as the “soapy” feel of the solid stuff with which we wash are the result of retained water and disappear in the anhydrous solid.

#### *The Characteristics of Soap Solutions*

The most obvious characteristic of a soap solution is the way in which it froths. Many impure liquids and solutions froth, but no pure substance. Aqueous solutions of amyl alcohol and basic iron acetate, for example, froth strongly; so do solutions of certain dyes, such as night blue. Diazotisation of commercial sulphanilic acid is complicated by the very persistent foam produced. In general, however, the stability of these foams is not of the same order as that of soap.

Soap solutions possess a marked detergent action. This is not due to alkali formed by hydrolysis as formerly supposed, for it has been shown that the actual amount of free alkali is quite small. Grease-free soot adheres to filter paper, but is removed by soap solution without any mechanical treatment. The soap seems to act by dispersing the soot to a very fine suspension, thus simulating true solution on a macroscopic scale.



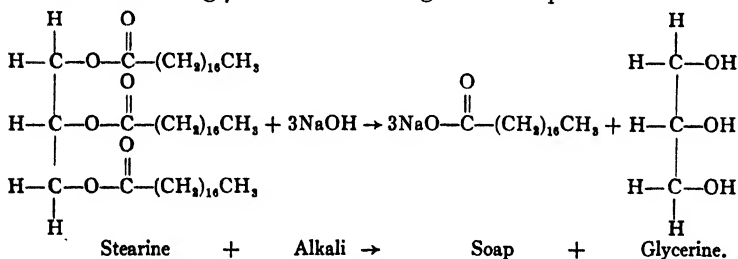
Soaps, even in very small quantities, lower the surface tension of water enormously. This surface activity, however, is not restricted to soaps, as many organic substances have the same action. They are hydrophilic colloids and also electrolytes.

Finally, it must be remembered that the characteristic properties of soap are developed only in aqueous solution, and not when dissolved in alcohol or other organic solvents.

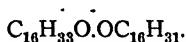
### *Preparation of Soap*

Commercial soap is prepared from vegetable and animal oils and fats. These are all esters, being mainly triglycerides.<sup>1</sup> They are named from the fatty radicle present; for example, glycerine tri-stearate is called "stearine." The most commonly occurring fatty acids are stearic, palmitic, and oleic. The natural products contain complicated mixtures of these esters,<sup>2</sup> and sometimes free fatty acid as well.

They are boiled with caustic soda, which forms soap and liberates glycerine according to the equation:



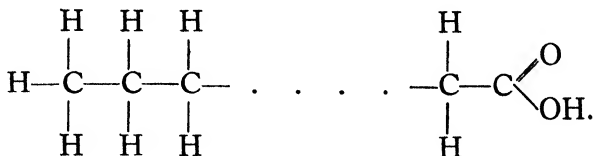
<sup>1</sup> A few animal fats are esters of monohydric alcohols containing the same number of carbon atoms as the fatty acid. For example, spermaceti is cetyl palmitate:



<sup>2</sup> Recent work (*Journ. Soc. Chem. Ind.*, **47**, 261 [1928]) suggests that mixed esters, containing one unsaturated and two different saturated fatty radicles, occur commonly.

### *The Origin of Saponaceous Properties*

Stearic and palmitic acids belong to the homologous series  $C_nH_{2n+2}O_2$  ( $n$  being any integer from 1 upwards), which is so important that it must be considered in some detail. It is better understood when the general formula is written:



All the naturally occurring members are straight chain compounds and, for some unknown reason, contain an even number of carbon atoms. The properties of the odd members of the series are practically unknown, although they can be synthesised fairly easily from the corresponding even number members containing one carbon atom less.

The names of the naturally occurring acids, the number of carbon atoms in the molecule, and their chief sources are:

	<i>n</i> .	
Acetic . . . . .	2 . . .	Vinegar.
Butyric . . . . .	4 . . .	Butter.
Caproic (hexoic) . . . . .	6 . . .	Goats' milk.
Caprylic (octoic) . . . . .	8 . . .	" "
Capric (decoic) . . . . .	10 . . .	" "
Lauric . . . . .	12 . . .	Laurel berries.
Myristic . . . . .	14 . . .	Nutmeg butter.
Palmitic . . . . .	16 . . .	Palm oil.
Stearic . . . . .	18 . . .	Suet.
Arachidic . . . . .	20 . . .	Arachis oil.
Behenic . . . . .	22 . . .	—
Cerotic * . . . . .	26 . . .	Chinese wax.
Melissic * . . . . .	30 . . .	Beeswax.

\* There is some doubt whether these acids are the 26 and 30 members or the 27 and 31.

The appearance of saponaceous properties is quite sudden. Colloid particles have been detected in solutions of caproates; the osmotic pressure of the potassium salts first shows peculiarities at caprylic. The electrical conductivity/concentration curve characteristic of the soaps first appears at lauric;<sup>1</sup> this acid is the first whose sodium salt has a definite emulsifying power; sodium caprylate has none.

The lowering of surface tension of water by the

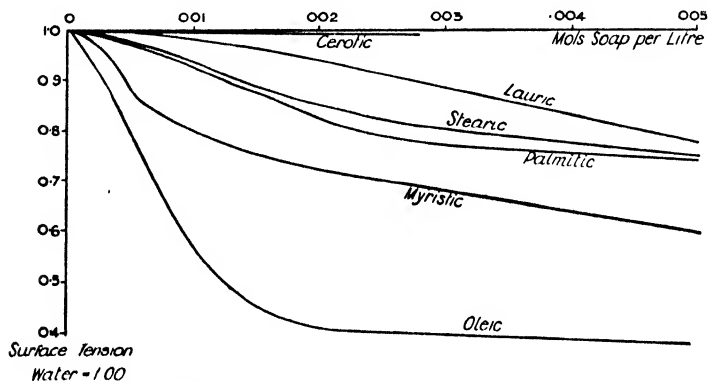


FIG. 5.—Relative surface tension of sodium salts of fatty acids.

sodium salts of the series has been thoroughly investigated by Lascaray<sup>2</sup> and Walker.<sup>3</sup> Their results (Figs. 5, 6, 7) show clearly that a certain length of chain is required to cause the surface activity characteristic of the soaps. The results for valeric and iso-valeric show that a straight-chain compound is more active in lowering the surface tension than its branched-chain isomer. A second result is that the activity decreases almost as rapidly as it appears. Walker's results show (Fig. 8), however, that it is incorrect to state definitely that a substance is or is

<sup>1</sup> See Fig. 44, p. 85.

<sup>2</sup> *Kolloid Zeit.*, **34**, 73 [1924].

<sup>3</sup> *Journ. Chem. Soc.*, **119**, 1521 [1921].

not a soap without specifying the temperature. For solutions of sodium arachidate and behenate appear to

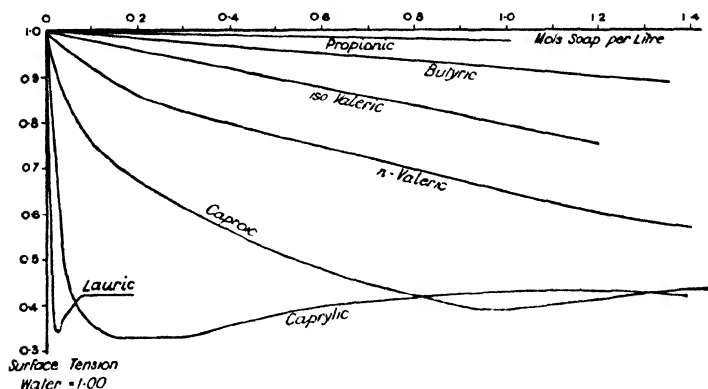


FIG. 6.—Relative surface tension of sodium salts of fatty acids.

become soaps at the boiling-point while lauric is losing its activity. It is curious how all the curves, except that

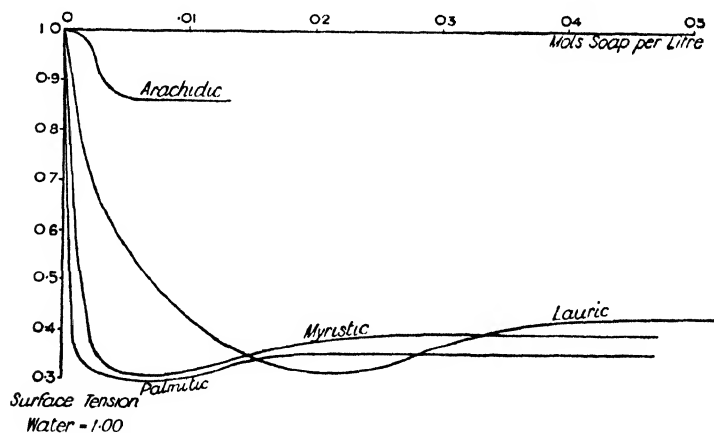


FIG. 7.—Relative surface tension of sodium salts of fatty acids.

of oleic acid, seem to be making for the quite artificial origin of the graph, namely, zero activity at 0° C.

The actual significance of these figures, obtained by drop-weight methods, is complicated by the fact that they do not agree with capillary-elevation results at low concentrations of soap. The time taken by a soap solution to reach its minimum surface tension has already been discussed. In the capillary-elevation method, there is ample time for the formation of the specific surface layer; on the other hand, in the drop-weight method, if the drop forms faster than the surface of minimum surface tension, it may pass and exceed the size corre-

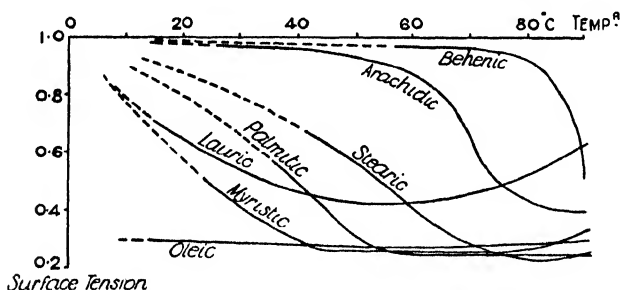


FIG. 8.—Dependence of surface activity of soaps on temperature.

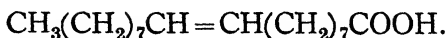
sponding to the static value. The result will be that the measured value of the surface tension will be too high. Comparison of White and Marden's<sup>1</sup> figures with those of Lascaray suggests that the latter are subject to this error at the low concentrations concerned.<sup>2</sup>

In addition to these higher homologues of acetic acid, a number of other substances form soap solutions. Of these, the most important is oleic acid. This substance is very widely distributed in Nature and, as the triglyceride, is the main constituent of olive oil. It is closely related to stearic acid, as it contains the same number

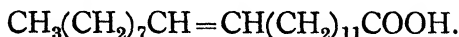
<sup>1</sup> *Journ. Phys. Chem.*, **24**, 617 [1920].

<sup>2</sup> Freundlich, *Colloid and Capillary Chemistry*, English trans., p. 534.

of carbon atoms but two hydrogen atoms less, having the formula:—

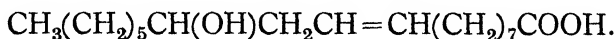


Being unsaturated, it occurs in two stereo-isomeric forms. The second is called elaidic: it does not, however, occur naturally. Corresponding to the  $\text{C}_{22}$  acid, behenic, is another pair of unsaturated isomers, brassidic and erucic acids, the tri-glyceride of the latter being the main constituent of rape oil. Their formula is:—



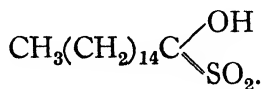
The position of the double bond is of interest in view of possible explanations of the origin of these substances in Nature.<sup>1</sup> From the naturally occurring oleic and erucic acids can be prepared the corresponding triple bond acids, stearolic and behenolic, both of which form soaps.

Other soap-forming acids are abrom-stearic and dihydroxy-stearic. Castor oil is mainly the tri-glyceride of ricinoleic acid, which may be regarded as a substituted derivative of oleic with the formula:—



Not only can variations take place in the chain without impairing the soap-forming properties of the substance, but to some extent the carboxyl group can be replaced.

The best-known example is cetyl sulphonic acid: <sup>2</sup>



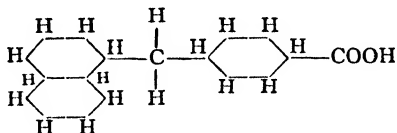
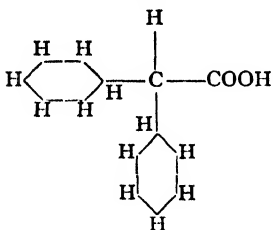
<sup>1</sup> Petroselic acid, a naturally occurring though rare isomer of oleic, has the double bond in the  $\epsilon$ ,  $\zeta$  position.

<sup>2</sup> Reychler, *Kolloid Zeit.*, **12**, 279 [1913]; Norris, *Journ. Chem. Soc.*, **121**, 2161 [1922].

This substance is particularly interesting since, not only are its alkali salts soaps but the free acid is soluble in water and forms a typical soap solution. Two similar soaps are para-octadecyl-benzene-sulphonic acid,<sup>1</sup> and the corresponding hexadecyl compound.

Finally, we have an entirely different type of substance, hexadecylamine hydrochloride, which dissolves in water to form a typical soap solution.

In addition to these substances which all contain a long hydrocarbon chain, there are a few cyclic acids known whose salts are soaps. For example, di-cyclohexyl-



acetic acid and  $\alpha$ -decahydro-naphthyl-cyclohexyl-methane-para-carboxylic acid.<sup>2</sup> The corresponding acids containing unhydrogenated rings do not form soaps.

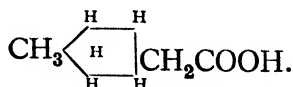
Somewhat similar are the higher naphthenic<sup>3</sup> acids obtained from kerosene distillation residues: these form soaps which are used commercially. They lather even better than vegetable-oil soaps, but their detergent action is inferior. They are a series, the first member of which is  $C_7H_{12}O_2$ . It is a methyl-cyclopentane-carboxylic acid and not, as is sometimes stated, hexahydro-benzoic acid. The higher members have longer alkyl groups in place of the methyl. They are usually named from their

<sup>1</sup> N. K. Adam, *Proc. Roy. Soc., A*, **103**, 676 [1923].

<sup>2</sup> Willstätter, *Chem. Zentr.*, **4**, 681 [1920].

<sup>3</sup> L. Gurwitsch, *Scientific Principles of Petroleum Technology*, trans. H. Moore, 1925, p. 90 *et seq.*

carbon atom content; thus the first member is called hepta-naphthenic acid. The sulphonated naphthenic acids also form good soaps. A naphthene-acetic acid is known:



The interest of these cyclic soap-forming acids lies in the shortness or absence of hydrocarbon chains. Where, however, a benzene ring, and no doubt a naphthalene too, is present it is only as a passenger in the molecule; there must be in addition a chain of sufficient length to possess saponaceous properties alone.

We see, then, that the commoner soaps consist of a long hydrocarbon chain, containing not less than 12 carbon atoms, with an active group at one end. The fatty acids are themselves insoluble in water, but their alkali salts dissolve to form soap solutions. It seems probable from the evidence reviewed here that the variety and number of substances capable of forming soap solutions is much greater than is usually suspected.

The solubility of soaps depends upon the nature of the base present. Potassium salts of the fatty acids are more soluble than the sodium. All the alkali metals form soluble soaps, as also do ammonia and its substituted organic derivatives. Krafft found many years ago that heptadecylamine erucate is soluble in water and forms a strongly doubly-refracting soap solution.

The heavy-metallic salts of the fatty acids are sometimes called soaps. This is rather misleading, as they are insoluble in water or very nearly so. Nevertheless, magnesium oleate at a concentration of 0.03 per cent. lowers the surface tension of water to 0.6 of its normal value.<sup>1</sup>

<sup>1</sup> Harkins and Brown, *Journ. Amer. Chem. Soc.*, **39**, 361 [1917].



The solubility of some of these metallic oleates in organic solvents is interesting in that the dry salts are practically insoluble, but a trace of water causes a high solubility. This occurs, for example, with lead oleate in ether and barium oleate in benzene.

The surface tension of a soap solution depends to some extent on the nature of the base present; Fig. 9<sup>1</sup>

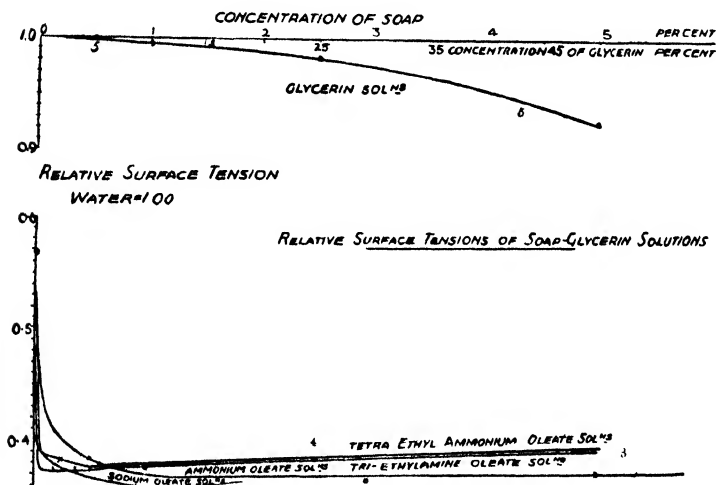


FIG. 9.

shows the surface tensions of a number of solutions used for soap-film work. The soap is dissolved in aqueous glycerine, the concentration of the latter being ten times that of the soap.

### *Soap Solutions for Films and Bubbles*

Oleic acid is used for the preparation of films and bubbles, usually as the sodium soap. This acid alone of

<sup>1</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **24** (1), 200 [1923]; *Collected Papers*, **2**, p. 1337.

the common ones forms solutions sufficiently mobile to allow free thinning and development of the films. Unfortunately, there is a serious drawback to its use; it is extremely difficult to obtain pure,<sup>1</sup> and it is somewhat chemically unstable. For long-lived films and bubbles all impurities must be rigorously excluded. Fatty acids other than oleic should not be present; especially the saturated acids palmitic and stearic, since they exert a profound influence, even in small quantities, on the oleate solutions. If, as is usually the case, the extent and nature of the adulteration is unknown it may be impossible for anyone, even the experimenter himself, to repeat an experiment.

Even with the purest materials and careful attention to details, it is sometimes impossible to retain experimental control over the solutions. As P. V. Wells remarks,<sup>2</sup> a solution will sometimes behave in a different manner on different days, although apparently under exactly the same conditions.

The use of sodium as base is by no means free from objection. Any excess of alkali is fatal to its film-forming capacity, while excess of oleic acid greatly increases the viscosity. Potassium oleate has no advantages and is still more viscous. Both these soaps deteriorate in the presence of carbon dioxide but are rendered much more workable by addition of a trace of ammonia.

Sir James Dewar<sup>3</sup> has made extensive use of ammonium oleate solutions; these, with tri-ethylamine oleate, are the best in every way for preparing films and bubbles, except, of course, where there is any possibility of considerable loss of the volatile bases.

<sup>1</sup> See Appendix I, p. 134.

<sup>2</sup> *Annales de Physique*, **16**, 82 [1921].

<sup>3</sup> *Proc. Roy. Inst.*, **24** (1), 199 [1923]; *Collected Papers*, p. 2, 1336.

Glycerine is usually added to soap solutions: it has the effect of stabilising films against local discontinuities arising from various causes. In Sir James Dewar's experiments to be described later, the concentration of glycerine was ten times that of the soap, the highest concentration commonly used being 5 per cent. soap in 50 per cent. of glycerine. The choice of a solution must

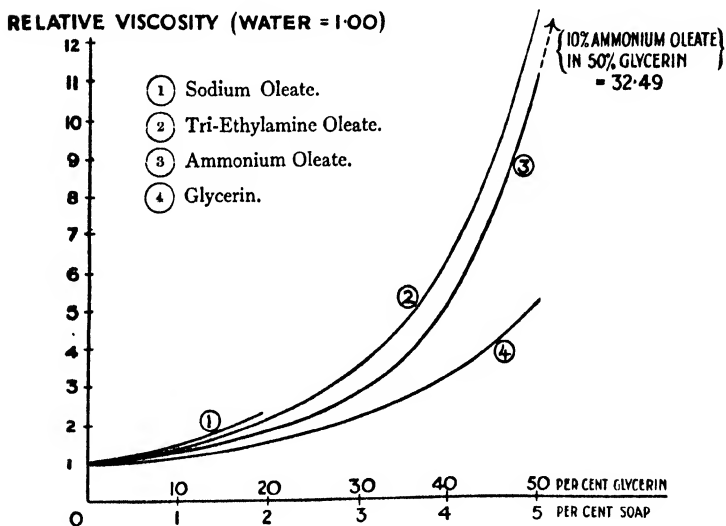


FIG. 10.—Viscosity of soap-glycerine solutions.

depend on the nature of the film or bubble required and the conditions under which it is expected to "live." Viscosity is an important factor, although we cannot assign any specific effect to it. Fig. 10 shows the variation of viscosity of some soap-glycerine solutions with increasing concentration.<sup>1</sup>

Fig. 11 shows the very marked effect of addition of oleic acid to a 5 per cent. ammonium oleate in 50 per

<sup>1</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **24** (1), 201 [1923]; *Collected Papers*, **2**, p. 1338.

cent. glycerine solution.<sup>1</sup> Addition of ammonia, on the other hand, only reduces the viscosity very slightly.

The viscosity of ammonium oleate solutions is complicated by the way in which these solutions can lose a large part of their combined ammonia without separation of oleic acid or the increase of viscosity to be expected

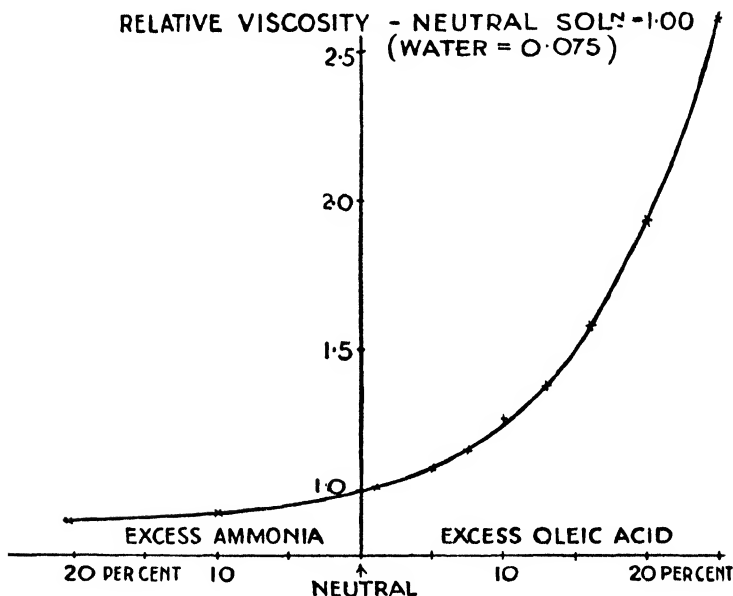


FIG. 11.—Viscosity of acid soap solution.

from Fig. 11. The actual increase of viscosity is quite small until the solution is re-neutralised, whereupon it sets to a jelly which only slowly reverts to the normal condition of the neutral solution at room temperature, If the jelly is heated it becomes normal at once.

For this reason films for open-air work should be

<sup>1</sup> Sir J. Dewar, *Proc. Roy. Inst.*, 24 (1), 201 [1923]; *Collected Papers*, 2, p. 1338.

prepared from tri-ethylamine oleate solution in preference to the more volatile ammonia.

Soap solutions are most satisfactorily prepared from free oleic acid. Sodium oleate freshly crystallised from absolute alcohol may be used, but is rather difficult to dissolve. Commercial sodium oleate should always be regarded with suspicion. The purest anhydrous soap decomposes even when kept in a sealed tube; a smell characteristic of burning vegetable oil develops. This is sometimes attributed to the formation of acrolein, the decomposition product of glycerine, which is really, however, quite a different substance.

Oleic acid should always be kept in a sealed tube.

A 5 per cent. ammonium oleate solution in 50 per cent. glycerine is best prepared for use either at full strength or diluted as required. Exact neutralisation being unnecessary, the solution is conveniently made up by volume.

10 c.c. oleic acid,<sup>1</sup>  
76 c.c. glycerine,  
54.4 c.c. water

are shaken into an emulsion and 32 c.c. of normal ammonium hydroxide added. This latter is simply prepared by diluting commercial .880 ammonia to one-twentieth strength.

For tri-ethylamine soap, 3.23 grm. of the base, freshly distilled over caustic potash (b.p. 90°), dissolved in 30 c.c. of water is used in place of the ammonia. Sodium and potassium oleates require to be exactly neutral; the acid must, therefore, be weighed out, and the calculated amount of standardised alkali added. Plateau's *liquide glycerique*, which is a convenient sodium oleate solution,

<sup>1</sup> The preparation of pure oleic acid is described in Appendix I (p. 134).

contains 1·89 per cent. of sodium oleate in 23·6 per cent. of glycerine. For its preparation from free oleic acid the following quantities are required:—

28·2 grm. oleic acid,  
100·0 c.c. normal caustic soda solution,  
300·0 c.c. glycerine,  
1200 c.c. water.

It is improved by a trace of ammonia; three drops of concentrated ammonia to the above amount.

## CHAPTER III

### SOAP FILMS

IF a wire frame is dipped into soap solution a film is formed across it when lifted out. But for the rigid peripheral support the film would contract to a spherical drop, under the influence of surface tension. This force, acting equally in all directions, keeps the film in a state of tension, and therefore plane. Conversely, we may consider what happens when a small hole is formed in a film. Surface tension will act around and normal to its circumference; the magnitude of this contractile force will therefore increase in proportion to the size of the hole, and the rate of disruption of the film will be constant. The actual speed is about 72 miles per hour.<sup>1</sup>

The circular form of a hole in a film as a result of the action of surface tension may be shown by the following experiment. A thread, double for part of its length, is attached to a wire frame which is dipped in soap solution and a film formed on it in the usual manner (Fig. 12A, Plate I). The part of the film between the double thread is then broken: the hole thereupon assumes a circular form (Fig. 12B, Plate I), since this entails the smallest area for the remainder of the film.

#### *Forms of Soap Films*

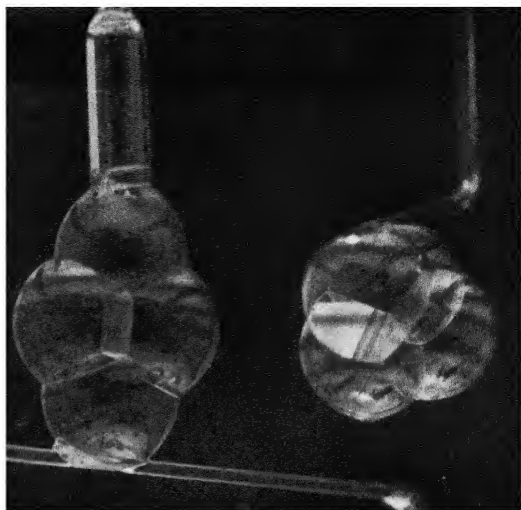
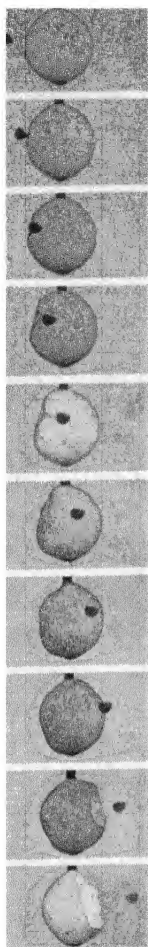
A bubble is, of course, a particular form of film. It is usually blown up from a plane film across a glass tube, which then serves to support its weight. Bubbles may be made to float in air by blowing them up with air

<sup>1</sup> *Fourth Report of British Association on Colloid Chemistry*, p. 48.





PLATE II.



(b)

(a)

FIG. 14. Coalescence of four bubbles.

FIG. 13. The passage of a pellet through a soap bubble.

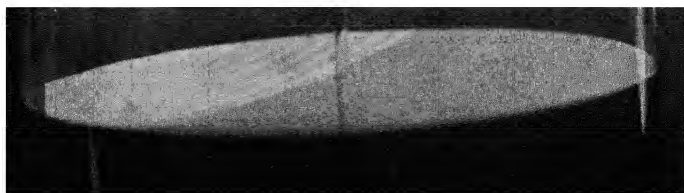


FIG. 17.—Large horizontal film.

containing some light gas such as hydrogen, or an air-expanded bubble can be floated on ether vapour.<sup>1</sup>

It has already been pointed out that a bubble contains its own support against the contractile force of surface tension; that is, the internal excess pressure. One result of this is that the tube through which a bubble is expanded must be closed, otherwise the bubble will quickly deflate itself. The expression of the air may be seen by the deflection of a candle flame held at the end of the tube.<sup>2</sup>

An interesting example of this indirect action of surface tension is given by the passage of a pellet through a bubble. As the projectile enters the bubble it draws a "neck" into the bubble behind it; this is then closed up by the outward push of the internal excess pressure. At its exit, the pellet draws out a similar neck; the internal excess pressure now prevents this from closing up, and the final exit of the pellet leaves a hole in the surface which, of course, leads to disruption of the bubble. Fig. 13, Plate II, shows some stages of this sequence of events; they are taken from the wonderful complete cinematographic record obtained by M. Lucien Bull at the Marey Institute. These photographs were taken at the rate of 3000 per second.

A spherical bubble can be drawn out to a cylindrical form, subject to certain reservations.<sup>3</sup> It is stable so long as its length is less than its circumference; when its length becomes more than  $\pi$  times its diameter it becomes unstable, develops a waist, and lapses into two spherical bubbles.

The internal excess pressure of such a cylindrical

<sup>1</sup> Boys, *Soap Bubbles*, p. 121.

<sup>2</sup> *Ibid.*, p. 54.

<sup>3</sup> See article on "Capillarity" in *Encyclopædia Britannica*, 10th edit., by Maxwell and Lord Rayleigh.

bubble is only half that of a spherical one of the same diameter. This may be seen by consideration of a plane through it normal to the long axis. Using the same symbols as before we have for equilibrium:

$$p \frac{\pi D^2}{4} = \pi D \sigma,$$

so that

$$p = \frac{4\sigma}{D} \quad . \quad . \quad . \quad (4)$$

whereas for a spherical bubble

$$p = \frac{8\sigma}{D}.$$

The experimental demonstration of this is described by Boys.<sup>1</sup>

Now the commonly occurring forms of film and bubble are not the single ones. A bubble coming into contact with the surface of the liquid from which it was formed coalesces with it, and is drawn into a hemisphere. Rain-drops frequently form such half-bubbles in puddles.

If two bubbles are brought into contact they will not unite. If, however, a drop of soap solution is introduced at the point of contact they immediately do so. Coalescence is also induced by a piece of electrically charged sealing-wax. It is suggested that the failure of the bubbles to unite is due to the presence of a thin cushion of air; a similar condition, in fact, to the spheroidal state. Mechanical and electrical forces act by hastening the effusion of this air. On the other hand, we have the undoubted fact that it requires a definite effort to break through the surface layer. And this is just what the first stage of coalescence consists of.

<sup>1</sup> *Soap Bubbles*, p. 60.

The form of these coalesced bubbles is governed by a simple rule. Only three planes can intersect along a line, and these planes will be equally inclined; that is at  $120^\circ$ . At any point, therefore, four edges and six films meet.

Fig. 14, Plate II, shows clusters of four coalesced bubbles; with this number two forms are possible, A being the stable one.<sup>1</sup> With larger numbers of bubbles the forms become rather complicated. Foam is a collection of irregular hexagons formed of bubbles of various sizes coalesced according to the rule stated. In such a mass, only the outer surfaces are curved to any extent. It is only at these surfaces, therefore, that there is a difference of pressure on the two sides. Contraction of the films by effusion of air is limited by this, although the whole mass is drained to the black stage very quickly by the numerous interconnected liquid channels.

The biological importance of films is considerable, though the present state of our knowledge of them is vague. The frequent occurrence of foam, sometimes of remarkable stability, as in tropical rivers, attests the widespread distribution of surface active substances such as saponin.<sup>2</sup> In this country it is more frequently found in beer.

A mass of foam may serve as a protective mantle to an insect, as in the familiar example of cuckoo spittle.

The line of intersection of three films is a channel

<sup>1</sup> Sir James Dewar, *Proc. Roy. Inst.*, **22** (2), 377 [1918]; *Collected Papers*, **2**, pp. 1215-1224.

<sup>2</sup> This and similar substances occur in many plants. In this country the common soapwort and the fruit of the horse chestnut are the best known sources. In parts of America the berries of *Sapindus saponaria* are used as a substitute for soap, while the bulb of *Chlorogalum pomeridianum* and the berries of *Limonia acidissima* serve the same purpose in California and Japan.

of liquid roughly triangular in shape. In a mass of foam this channel holds more liquid than the amount present as actual films. Solid bodies are drawn into these channels, a circumstance which adds to the stability of the foam.

The boundary of every film consists of such a channel.

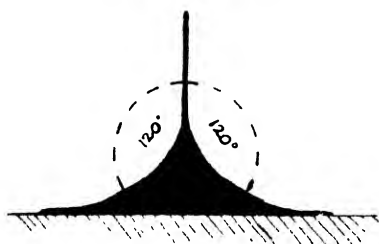


FIG. 15.—Gibbs' ring.

In this connection they have been investigated by Willard Gibbs.<sup>1</sup>

A simple case is that of a film meeting a solid surface normally. We really have three films which meet according to the rule at equal angles. This leaves a triangular channel filled with soap solution (Fig. 15). The size of this channel depends on a number of factors, but, if drained, may become very small indeed.

It is an important factor in the life of a film,<sup>2</sup> stabilising it against shock by lubricating its movements in its container. On the other hand it is a source of weakness in that it may attack the glass or other material with which it is in contact, and so liberate substances injurious to the film.

### *The Preparation of Films and Bubbles*

A necessary preliminary to the investigation of the properties of soap films and bubbles is the development of a technique for their preparation and maintenance. All who have worked in this field know the difficulty of keeping films long enough to make observations on them. Sir James Dewar has shown what can be done in this

<sup>1</sup> *Collected Papers*, 1, p. 309.

<sup>2</sup> See pp. 46, 77.

direction by systematic attention to details. The methods described in the following pages are mainly those worked out by him.

Soap solution must be pure. Impure solution means untrustworthy films; such results as are obtained from solutions containing unknown impurities only lead to confusion. A number of substances can be added to soap solution without serious detriment; for example, potassium nitrate and sodium sulphate have been added to increase the electrical conductivity, while sugar and various dyes have been added for other purposes. Nevertheless, if longevity is desired, all such additions should be regarded with suspicion. Glycerine is the only substance known definitely to improve soap solutions.

The most dangerous impurities are those likely to find their way into solution unnoticed.

Carbon dioxide should be excluded, while grease and floating particles in the atmosphere are equally dangerous.

The simplest way to form a film is to dip a wire frame into a suitable soap solution; on lifting it out, a thick film forms across it. Platinum or platin-iridium are the most satisfactory materials for the ring, as they can be cleaned perfectly by heating to redness and are not attacked by soap solution.

If, however, it is desired to keep the film for some time, the simplest way is to "throw" it in a bottle. In Sir James Dewar's experiments, a hard glass bottle of about 19 cm. diameter was used. After cleaning thoroughly (the efficient but somewhat dangerous mixture of 4 parts of concentrated nitric acid and 1 of absolute alcohol is used) the bottle is thoroughly rinsed in running water and then in freshly distilled. About 150 c.c. of 2.5 per cent. ammonium oleate in 25 per cent. glycerine solution is then added, and the bottle closed with a

well-ground stopper. To obtain a film, the solution is run all over the interior of the bottle; it is then held on its side while the solution is thrown with a regular swirling motion across the part of the bottle where the film is required. With a little practice it is easy to obtain a film without a mass of foam as well. The advantage of this method of preparation is that once the solution is in the bottle there is no chance of contamination. Consequently, such films last for very long periods. One shown at Sir James Dewar's lecture in January 1917 was still in existence a year later. More recently, a film lasted in the same bottle for more than three years. The development of a film—the production of colour and the appearance of the black—is conveniently observed by fixing a piece of black paper half-way round the bottle and up to the level of the film with a similar piece of white above it.

Larger films cannot be prepared in this way. Films 56.5 cm. diameter were obtained<sup>1</sup> in a cylindrical glass vessel by expansion of a hemispherical bubble from solution at the bottom. Fig. 16 shows the experimental arrangements. The globe is thoroughly cleaned and fitted with a well-steamed rubber bung which carries the tubes shown. Air, freed from carbon dioxide by passing through two towers filled with caustic potash and filtered from solid particles by two more towers filled with cotton-wool moistened with glycerine solution of the same concentration as the soap solution to be used, is blown in through *A*. This is continued until the globe is optically empty. (If there is solution already in the globe the Tyndall cone will show a dense mist; dust particles are, however, easily detected, and the air current

<sup>1</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **22** (1), 188 [1917]; **22** (2), 361 [1918]. *Collected Papers*, **2**, 1207.

continued until they have all been removed.) Soap solution is then added through *C*, and the dropping

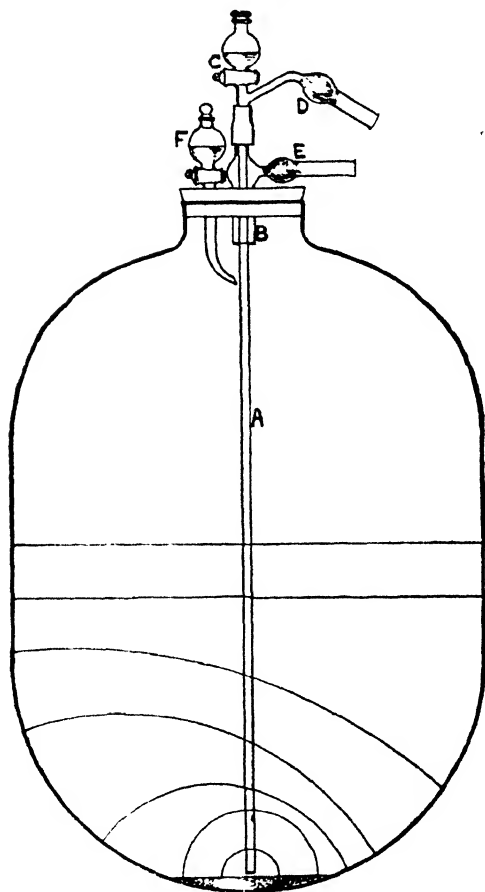


FIG. 16.

funnel *F* is also filled. Five per cent. ammonium oleate in 50 per cent. glycerine was always used.

To obtain a film, the globe is tilted and the solution run all over the walls, while the tube *A* is wetted with



solution from *F*. The air current is started slowly, and the tube *A* momentarily dipped below the surface of the solution at the bottom of the globe. Two or three bubbles are formed, one of which is expanded, the rate of the air current being increased for this purpose. The diagram

shows the successive stages of the film. When it has reached about half-way up the globe, the air supply is cut off; the inlet tube *D* and the exit *E* are closed with soda-lime tubes. Both sides of the film must be kept at the same pressure, otherwise barometric fluctuations cause the film to move up and down the vessel. Any such movement leads to speedy rupture once the walls are drained from excess soap solution. Fig. 17, Plate II, shows the appearance of such a film a few days after preparation. The form of the colour bands shows that the film is slightly tilted. Films of this size lasted for 40 days.

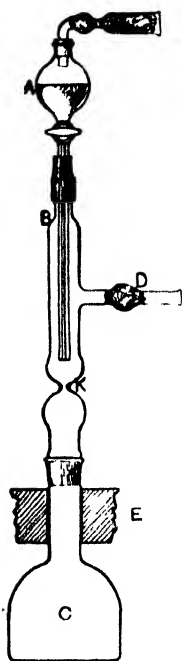


FIG. 18.

If the nozzle (about 8 cm. diameter) shown in Fig. 18 is substituted for the blowing-tube *A*, bubbles are conveniently blown in this apparatus.<sup>1</sup> The globe is cleaned as before. The reservoir *A* is filled with soap solution. Five per cent. ammonium oleate in 50 per cent. glycerine was usually employed, but  $3\frac{1}{2}$  in 33 was even better when tried; more dilute solutions do not give sufficiently stable bubbles.

Some of this solution is run down the nozzle until it is thoroughly wet. The air supply is started slowly; it expands the drop of solution remaining at the con-

<sup>1</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **22** (2), 367 [1918]; *Collected Papers*, **2**, 1211.

striction  $K$  into a plane film which travels down the nozzle. Several drops of solution are now dropped at intervals on to  $K$ , the air current being momentarily interrupted by pinching the rubber supply-tube attached to  $D$ . In this way the nozzle is filled with a mass of foam which is then blown out and hangs on to the bubble formed from the last drop. The air supply is now stopped, and about 10 c.c. of solution run down the nozzle. The air is restarted and the drop of solution at  $K$  expanded into a film and blown down the nozzle. When it reaches the end it displaces the bubble and froth which, weighted by the solution just run down, fall off. The clean film remaining is blown up into a bubble as large as required. The air supply is then stopped and a single drop of solution let fall on to  $K$ ; the air supply is then started again slowly, and the film formed is blown down to the end of the nozzle to close the bubble.  $D$  and the exit tube (not shown) are then closed by rubber bungs.

These bubbles were not usually expanded beyond 40 cm. diameter, and at that size lasted for very long periods. For example 42, 63, and 55 days, while 30 cm. ones lasted even longer, 85 and 108 days.<sup>1</sup>

The bubbles were sometimes drained by a fluted glass rod hung by a platinum wire or silk thread from  $K$ . These fluted rods were made by drawing out a bundle of glass rods in the blowpipe until the diameter was reduced to about 2 mm.

With the apparatus just described chains of bubbles can be blown by interrupting the air current periodically and dropping solution on to  $K$ .

Smaller bubbles, up to 25 cm. diameter, are most conveniently blown in 12-litre aspirators. A smaller

<sup>1</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **22** (1), 186 [1917]; *Collected Papers*, **2**, 1182.

nozzle about 4 cm. diameter is used, and a drainage rod can be inserted through the bottom tubulure.

Apparatus for blowing bubbles under both increased<sup>1</sup> and reduced<sup>2</sup> pressure has been described by Sir James Dewar.

### *The Life History of a Soap Film*

We may reasonably speak of the life history of a film or bubble, since all films pass through a regular cycle of changes and, sooner or later, collapse. The extent of their development depends, of course, on the length of their lives. The chief task of the experimenter is to preserve them from contamination, mechanical shock, and sudden large temperature changes; the film does the rest.

The fundamental change is the thinning which ultimately results in the formation of the so-called "black spot." This is the thinnest possible film.<sup>3</sup> It is only in the last few years that this change has been thoroughly observed, and the old idea that thinning led to rupture disproved.

The thinnest films are, in fact, remarkably stable. All liquid films thin; the black film is the limit beyond which further thinning is impossible. In this respect, therefore, the black film is the only stable film. But this must not be taken, as it has been, to mean that the black is more resistant to mechanical shock than the thicker coloured film, for it is really much less so.

When a film has reached the black stage it is permeable by air. In a bubble, the internal excess pressure causes

<sup>1</sup> *Proc. Roy. Inst.*, **22** (2), 403 [1918]; *Collected Papers*, **2**, 1241.

<sup>2</sup> *Proc. Roy. Inst.*, **22** (1), 196 [1917]; *Collected Papers*, **2**, 1178.

<sup>3</sup> Under certain circumstances, described later, more than one thickness of black is formed. The thicker blacks, however, are ephemeral and give place to the thinnest.

effusion of air through its walls until completely deflated to a plane film across the nozzle (see p. 75). Theoretically a plane film is "immortal." Actually they usually meet with some misfortune before reaching any great age.

It is possible to give an outline of the life history of a film, but numberless minor variations occur due to factors not under experimental control. In fact, no two films behave in exactly the same manner. Many, of course, never reach the "senile" stage of complete blackness.

All films and bubbles when first formed are thick and colourless. Thinning sets in immediately, and colour soon appears as a horizontal band at the top of a vertical film and as a disc at the centre of a horizontal one. Pale pink and green bands appear imperceptibly; these increase in breadth and brilliance until the purer colours of the lower orders of Newton's scale blaze out. Finally there appears the black spot. This then invades the whole film.

It is well known that the colour of the soap film is not intrinsic but due to interference between the rays of light reflected from the two faces. The simplest case is that of a film illuminated by monochromatic light. It appears to be traversed by alternate bright and dark bands which become narrower and less brilliant as the thickness increases. The production of these bands is easily explained by the wave theory of light. A ray of light  $AB$  (Fig. 19) falling on the film is divided into two parts, one being reflected along  $BC$  and the other refracted into the film, internally reflected at  $D$ , finally emerging along  $EF$ . Draw  $EP$  perpendicular to  $BC$ ;  $EP$  is parallel to the wave-front of the light entering the observer's eye. Draw  $BM$  perpendicular to  $DE$ ; continue

$ED$  to  $L$  so that  $DL = DB$ . Then  $LB$  is perpendicular to the film and equal to twice its thickness,  $\theta$ .

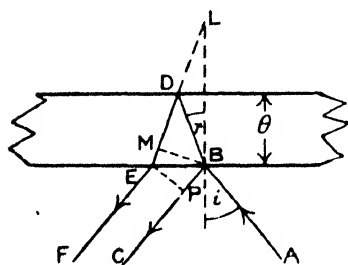


FIG. 19.

Now the difference of path of the internally and externally reflected rays is:—

$$BD + DE - BP,$$

which may be written:—

$$LM + ME - BP.$$

Allowance must be made for the reduction of the velocity of the ray in its passage through the liquid film; so that we have for the retardation of the internally behind the externally reflected ray

$$\mu(LM + ME) - BP$$

( $\mu$  is the refractive index of the film).

But  $\frac{ME}{EB} = \sin r$  and  $\frac{BP}{EB} = \sin i$ ;

therefore  $\frac{BP}{ME} = \mu \left( \text{since } \mu \text{ is defined as } \frac{\sin i}{\sin r} \right).$

The retardation is therefore  $\mu LM$ .

But  $LM = 2\theta \cos r$ , so we finally get the value

$$2\mu\theta \cos r \quad . \quad . \quad . \quad (5)$$

Now  $AB$  is being reflected at the surface of an optically denser medium; there is consequently a node at  $B$ , and  $BC$  differs in phase from  $AB$  by  $\frac{\lambda}{2}$ . If, then,  $2\mu\theta \cos r = \frac{\lambda}{2}$  or an odd multiple of  $\frac{\lambda}{2}$ , then  $BC$  and  $EF$  will reinforce one another. If, on the contrary,  $2\mu\theta \cos r = \lambda$  or an

integral multiple, then  $BC$  and  $EF$  will differ in phase and a dark band will result.

This is expressed more clearly by saying that the film appears dark when  $\mu\theta \cos r$  is an even multiple of  $\frac{\lambda}{4}$ , and bright when an odd one.

The general condition for interference is given by the equation

$$\mu\theta \cos r = \frac{n\lambda}{4} \quad . \quad . \quad . \quad (6)$$

Reinforcement takes place for odd integral values of  $n$  and extinction for even (including zero).

Illumination by white light produces more complicated interference phenomena. In an infinitely thin film the retardation of the internally reflected ray is negligible; the rays  $BC$  and  $EF$  therefore differ in phase by  $\pi$ , the reflection phase change of  $BC$ , and the film appears dark. The black film is so thin that extinction is almost complete, though not quite. As the thickness increases, we should expect to see a bright band corresponding to the thickness of  $\frac{\lambda}{4}$ . This would occur for the violet first, and then the blue, green, and so on through the spectrum in order of increasing wave-length. However, this separation of colours does not occur.<sup>1</sup> Actually, as the thickness increases, the film appears grey and then silvery white. Colour first appears as pale yellow when the violet approaches its minimum corresponding to the thickness of  $\frac{\lambda}{2}$ . Taking the refractive index of the film as 1.4, this

<sup>1</sup> P. V. Wells (*loc. cit.*, p. 23) suggests that the small luminosity of the violet end of the spectrum is the reason for this. I think the main cause is the finite, and often extensive, size of the source of illumination.

is about  $150 \mu\mu$ <sup>1</sup>: the film then appears bright golden. As more of the blue is cut out the film passes through amber to magenta. The green is at its second minimum at about  $190 \mu\mu$ , which corresponds to this shade of red. The red itself does not reach its second minimum until about  $250 \mu\mu$ , by which time the blue has reached its second ( $n=3$ ) maximum; the film therefore appears bright blue. Before this blue and after the magenta is a narrow strip of violet whose thickness is  $210 \mu\mu$ . As the thickness increases, the blue becomes tinged with yellow, turns green,  $290 \mu\mu$ , and then pure orange yellow,  $340 \mu\mu$ . This is followed by bright crimson shading into rich purple,  $390 \mu\mu$ , followed by some more blue. The next stage is a peculiarly vivid emerald green,  $450 \mu\mu$ , which assumes a yellowish tinge with increasing thickness. The final part of the colouration consists of a series of alternate carmine and green bands; the first pair are very brilliant,  $540$  and  $590 \mu\mu$ , after which they become progressively paler until the fifth pair is only just distinguishable from the white film. At this stage the film is about  $1500 \mu\mu$  thick. The complete list of thicknesses of various colours is given in Appendix II.

The remarkable character of these colours is most fully appreciated by watching the thinning of a film and attempting to write down a descriptive list of them as they appear.

It is clear from the reasoning outlined above that we cannot expect the presence of the pure colours of the spectrum, and if we consider equation 6 the reason for

<sup>1</sup>  $1 \mu\mu$ ; 1 millimicron is equal to a thousandth of a micron.

$1 \mu$ ; 1 micron „ a thousandth of a millimetre.

1 mm.; 1 millimetre „ a thousandth of a metre.

$1 \mu\mu$  is therefore  $10^{-6}$  mm. or  $10^{-9}$  metre.

1 Å.U; 1 Ångström Unit or a tenth metre is  $10^{-10}$  metre and, therefore, equal to a tenth of a  $\mu\mu$ .

the decrease of the purity and brilliance of the colour as the thickness increases becomes clear. When  $\theta$  is fairly large, the equation may be satisfied by two or more values of  $\lambda$ .

Spectroscopic analysis of the light reflected from a thinning film makes this point clearer. An absorption band will be formed if the thickness of the film opposite the slit is  $\frac{n\lambda}{4\mu}$  (for light at normal incidence and even values of  $n$ ). Now the thickness may be such that higher orders of absorption bands of other wave-lengths are formed also. Thus the general equation<sup>1</sup> for the formation of absorption bands at any thickness is

$$\theta = \frac{n\lambda_1}{4\mu_1} = \frac{(n+2)\lambda_2}{4\mu_2} = \frac{(n+4)\lambda_3}{4\mu_3} \quad (7)$$

( $n$  being an even integer).

The thinning of a film is very striking when viewed spectroscopically.<sup>2</sup> The thick newly formed film reflects a continuous spectrum. As thinning proceeds, a succession of dark bands moves rapidly across the spectrum from the red to the violet end, becoming farther and farther apart as the thickness decreases. The general occurrence of a number of absorption bands throughout the spectrum is the cause of the faintness of the higher orders of colour as compared with the more specific absorption in thinner films.

In the ordinary course of events, a film is not viewed at normal incidence. In estimating its thickness from the colour, correction must be made for  $\cos r$ .<sup>3</sup> A small

<sup>1</sup>  $\mu$  varies with  $\lambda$ ; for water the variation is only about 1 per cent. over the whole visible spectrum.

<sup>2</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **24** (1), 205 [1923]; *Collected Papers*, **2**, 1340.

<sup>3</sup> For the value of this correction, see Appendix II.



change in the angle at which a soap film is viewed causes striking colour variations.

We have a similar state of affairs when a film is viewed by transmitted light, with the important exception that the ray  $BC$  suffers no reflection phase change. The difference of phase of  $BC$  and  $EF$  is therefore

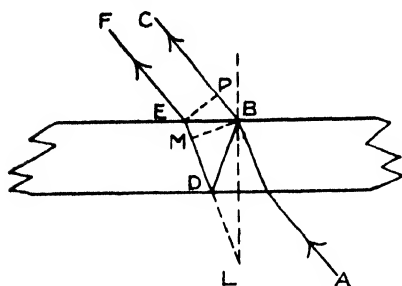


FIG. 20.

$BD + DE - BP$  (Fig. 20), which is obviously the same as in Fig. 19; that is,  $2\mu\theta \cos r$ .

For transmitted light, then, an infinitely thin film in which there is no appreciable retardation of the internally reflected ray, there is no

difference of phase between the rays  $BC$  and  $EF$ . The film therefore appears bright. As  $\theta$  increases, a dark band first appears when the retardation is equal to  $\frac{\lambda}{2}$ , that is when the thickness is such that

$$2\mu\theta \cos r = \frac{\lambda}{2} \quad . \quad . \quad . \quad (8)$$

In other words, the condition for darkness is that  $n$  should be odd and for reinforcement even in the equation:

$$\mu\theta \cos r = \frac{n\lambda}{4} \quad . \quad . \quad . \quad (6)$$

This is just the opposite to the conditions for reflected light, and may be stated more generally as:—"the colours of a film viewed by reflected and transmitted light are complementary."



PLATE III.

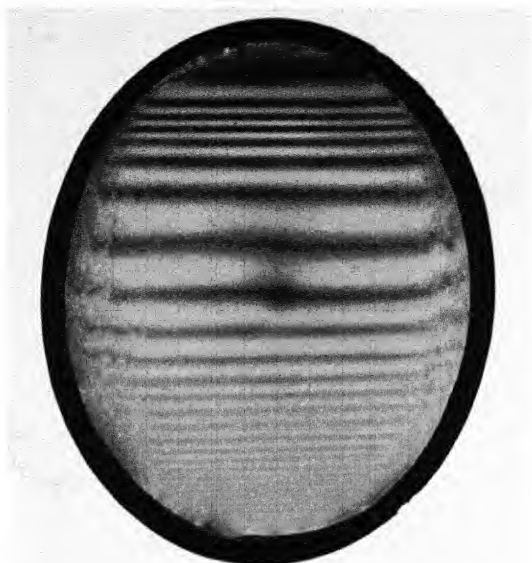


FIG. 21.—Thick banded film.

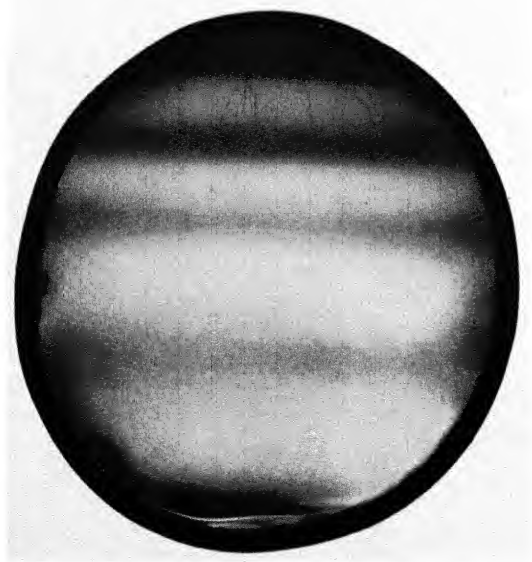


FIG. 22.—Later development of banded film.

Fig. 21,<sup>1</sup> Plate III, shows the appearance of a newly formed film illuminated by light filtered through a cell of potassium bichromate solution; that is nearly monochromatic orange light. The number of orders of interference bands is much greater than would have been visible with white light. Fig. 22, Plate III, shows a later stage in the development of the film; the small thickness gradient is seen from the smaller number and wider spacing of the bands. The sharp boundary between the black forming at the top and the next thicker part of the film is clear.

This sharp boundary is characteristic of the black and involves a large step-up in the thickness of the film, the adjacent part being anything from ten to a few hundred times as thick as the black. In a horizontal film the black first appears as a tiny circular disc which, as Perrin remarks, looks just like a hole punched in it.

It was formerly believed that the appearance of this "black spot" was necessarily a prelude to rupture. The earlier workers in this field had good reason for their belief, as their films always did break as soon as the black spot appeared. This was, however, due to the impurity of their soap solutions and to their failure to exclude contamination. Provided the film does not break, the black spot increases in area until it has invaded the whole of it.

In a vertical film the black boundary is, of course, a horizontal line. This line and the coloured bands show remarkable mobility in the plane of the film.

The rate of thinning of a vertical soap film of any given thickness is very much faster than the rate calculated from the fall of a sheet of liquid between two

<sup>1</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **24** (1), 204 [1923]; *Collected Papers*, **2**, 1340.

plates at the same distance apart. Further, there is no obvious reason why a horizontal film should thin as it

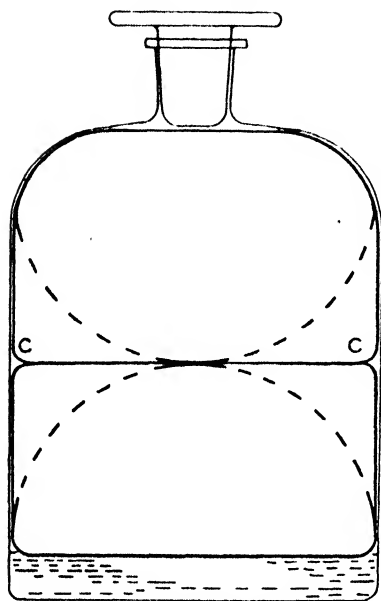


FIG. 23.—Thinning of a horizontal film.

A truly horizontal film, therefore, thins from the centre outwards. Actually, of course, the Gibbs' ring never reaches any great size, as the excess liquid drains away down the side of the bottle.

At first sight the form of a horizontal film is not what we should expect. It is convex upwards; we should rather expect it to be concave with a pendulous drop of excess liquid at the centre. The convexity is also a result of the

does at all. The Gibbs' ring<sup>1</sup> is responsible for this activity. Fig. 23 shows the form of a horizontal film in a bottle; the film surfaces try to reduce their area by reduction of the curvature where they meet the bottle, the ideal state being shown by dotted lines. The only way in which the curvature at C can be reduced is by addition of liquid from the film into the Gibbs' ring.

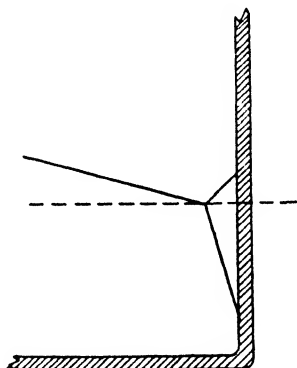


FIG. 24.—Curvature of film at Gibbs' ring.

<sup>1</sup> See pp. 32, 77.

Gibbs' ring. In a newly formed film this is large; its weight produces distortion as shown in Fig. 24; for the three films to meet at equal inclination the film must slope slightly upwards; it is, in fact, convex. Thinning takes place from the centre; the colour appears as circular rings and the black as a circular "spot."

Fig. 25 shows an enlarged diagrammatic view of the Gibbs' ring formed at the junction of a film and a wire ring. Here again the curvature at *C* can only be reduced by suction of liquid from the film into the channel. The powerful attraction of liquid into the Gibbs' ring is shown by allowing a drop of liquid—for example, barium

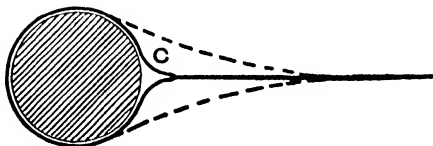


FIG. 25.—Sectional view of Gibbs' ring.

chloride solution—to fall on to the surface of a horizontal film. It will run about the surface until it reaches the neighbourhood of the Gibbs' ring into which it is immediately sucked, breaking the film as a result. If a horizontal film is examined microscopically, the outer limit of the Gibbs' ring is sometimes visible as a ring of light. This suggests that we have not two films which approach asymptotically but three, meeting at this point at  $120^\circ$  (see p. 130).

The effect of the Gibbs' ring is shown by the rate of blackening of a bubble or film. The vertical depth of black is plotted against time; the fall of the boundary being called the "black fall." When a bubble is first blown it is only feebly coloured; thinning, however, goes on quickly, and shortly a collar of black about 3 mm.

deep appears around the nozzle on which the bubble hangs. This is the direct result of the upward suction of the Gibbs' ring. The black collar does not increase in area until the coloured part of the bubble has become quite thin and the downward drainage operative. Blackening then proceeds at a steady rate until the bubble is

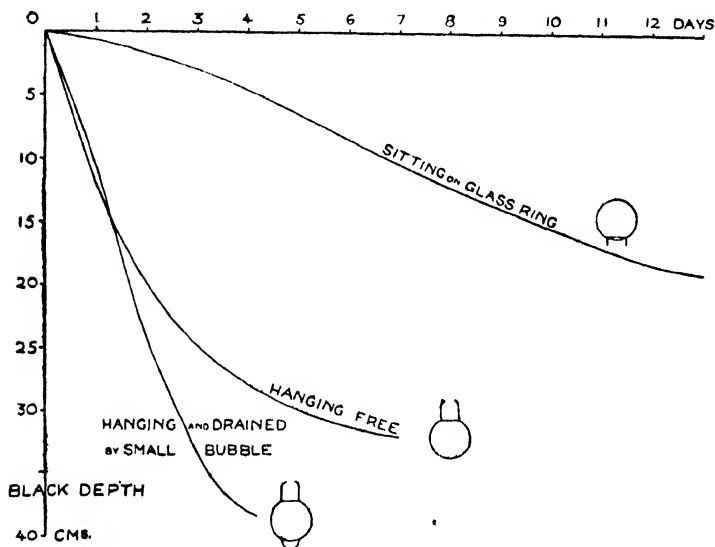


FIG. 26.—Black fall in bubbles.

about half black; after this the rate gradually slows up (Fig. 26).

If the bubble, instead of hanging from a nozzle, sits upon a ring, then, after removal of the blowing-tube, the only Gibbs' ring is at the bottom of the bubble and so aids thinning continuously. The rate of blackening does not therefore fall off as in the case of the hanging bubble, but, if anything, increases. The third curve in Fig. 26 shows the rate of black fall for a bubble drained by another smaller one attached to it. This is the most

efficient way of draining a bubble, since the Gibbs' ring between the bubbles is itself continuously drained through the small one. In this figure the actual rates of black fall are not directly comparable.

Various deviations from these characteristic curves occur. Fig. 27 shows some black falls in small hanging bubbles in which sudden increases of the rate took place. The cause of this will be dealt with later. Occasionally

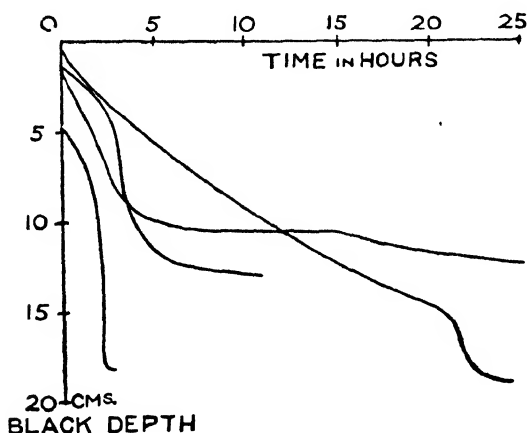


FIG. 27.—Abnormal black falls.

a bubble will blacken regularly but very much faster than usual; the reason for this is not clear.

On the other hand, bubbles sometimes partially thin and then develop considerable rigidity. The black boundary no longer remains a sharp horizontal line; the colour bands become streaky and no further thinning takes place. This effect has been traced to the influence of impurities in the soap solution, especially palmitic and stearic acids.

So far, it has been stated that the boundary between



the black and the next thicker part of the film is always sharp and involves a large increase of thickness. This statement must be modified somewhat, since more than one grade of black may be formed. Newton first observed two grades of black (see Fig. 39, Plate X, p. 60). Reinold and Rücker<sup>1</sup> also observed the existence of a second black, and made tentative measurements which suggested that the thickness of the first order was half that of the second. They also observed a general increase of thickness near the boundary of the black which caused distortion of their interferometer fringes. Later, Johonnott<sup>2</sup> found no less than five grades of black by microscopic examination of a soap film, the first three to appear being very evanescent. Working with films on frames in exhausted tubes, Sir James Dewar<sup>3</sup> was able to observe the rate of coalescence visually; Fig. 28 shows this for the first three orders. Solutions containing glycerine, however, usually form only one black.

### *Abnormal Developments*

In the last section the steady development of a film has been described. It has been emphasised that the essential condition for this series of changes is that the film should be kept undisturbed. Even so, abnormal developments occur. Reinold and Rücker<sup>4</sup> mention the occasional occurrence of an abnormal tumultuous blackening; Johonnott,<sup>5</sup> working with films in closed vessels,

<sup>1</sup> *Phil. Trans.*, **177**, 627 [1886].

<sup>2</sup> *Phil. Mag.*, (6), **11**, 753 [1906]; Perrin, *Annales de Physique*, (9), **10**, 160-163 [1918].

<sup>3</sup> *Proc. Roy. Inst.*, **21** (3), 806 [1916]; *Collected Papers*, **2**, 1171.

<sup>4</sup> *Phil. Trans.*, **177**, 677 [1886].

<sup>5</sup> *Phil. Mag.*, (6), **11**, 746 [1906]; P. V. Wells, *Annales de Physique*, **16**, 83 [1921].

found that he could convert the second order of black into the first by a small sudden increase of the pressure of the surrounding atmosphere.

In this section I shall describe a number of develop-

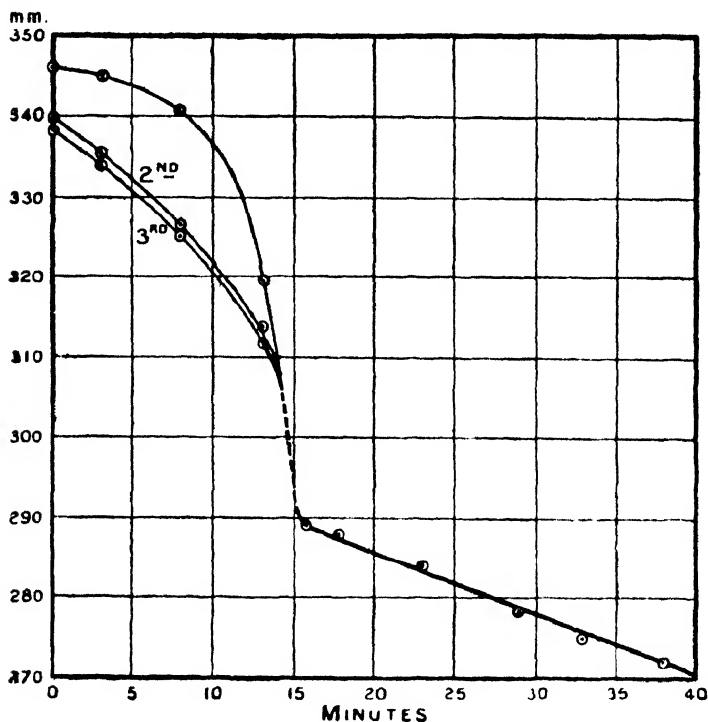


FIG. 28.

ments which are to be regarded as abnormal, in that definite stimulation is required to produce them although this stimulation is not always under experimental control.

The study of the development of a film under various conditions requires suitable apparatus for preserving the films and for stimulating the thinning processes.

Fig. 29, Plate IV, shows the apparatus used by Sir James Dewar.<sup>1</sup>

The film is contained in an air-tight box made of sheets of plate glass 1 ft. square. Holes are drilled in the top sheet to carry the fittings required. A vertical film is formed on a wire ring of about 4 in. diameter; this is attached to a glass rod which moves up and down through a glass stuffing-box packed with cotton-wool moistened with glycerine and held in a rubber bung in the centre hole. Solution is contained in a glass dish at the bottom of the cube. To obtain a film, the ring is lowered into the solution and then lifted up again, care being taken to avoid contact with the side of the glass dish. It is then turned at an angle of  $45^\circ$  to the sides of the cube. Illumination is provided by a parallel beam from an arc (in the box behind the cube), which is reflected from the film into the camera on the optical bench. This also carries a photometer for comparison of the intensity of the light reflected from different parts of the film with a standard source. For visual examination, the image is projected on to a large white screen by a suitable lens. The film can be drained by a bundle of fine platinum wires attached to one of the glass rods. Glass tubes, either drawn out to a point or sealed with a perforated platinum disc, are held by the other glands in the cover. These tubes are so arranged that an air jet can be directed to any part of the film as desired. Air is supplied to them from the constant-pressure aspirator, shown in the photograph, at a pressure of a few centimetres of water.

An air jet directed normally at the film forms a quadruple vortex pattern; at glancing incidence only twin vortices are produced. Typical examples are shown in

<sup>1</sup> *Proc. Roy. Inst.*, **24** (1), 222 [1923].

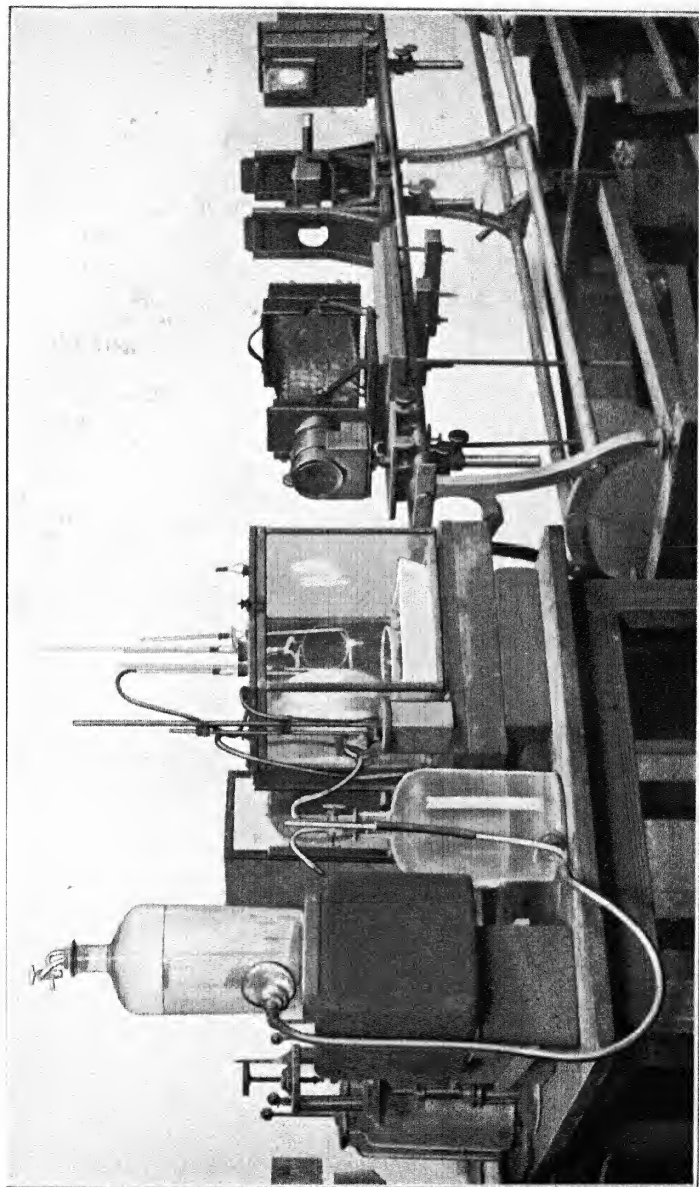


FIG. 29. Sir J. Dewar's apparatus for the study of liquid air.





PLATE V.



FIG. 30A.

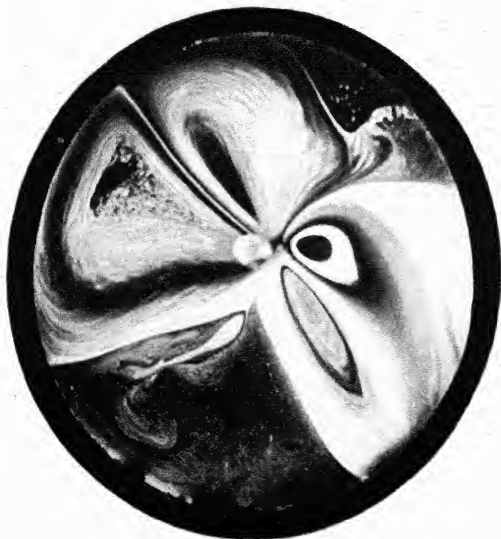


FIG. 30B.

Vortex patterns produced by air jets.





PLATE VI.



FIG. 31A.



FIG. 31B.

Analysis of vortex stream by electric spark.



PLATE VII.



FIG. 32A.—Quiet vortex pattern.



FIG. 32B.—Same disturbed by whistle.

Fig. 30A and B, Plate V. These air jets aid thinning by centrifugal action; black appears as a heart to the vortices and gradually increases in area. Of course, if the jet is directed at the bottom of the film thinning does not proceed very far, since liquid is continuously carried up into the vortex. These photographs were taken with an exposure of a thousandth of a second; exposure by an electric spark resolves this streaming motion into a procession of droplets (Fig. 31A and B, Plate VI).

It is interesting to note that these low-pressure air jets were found to be sensitive to sound, the film acting as an exceedingly efficient indicator by virtue of the startling changes produced by very small fluctuations of air pressure. Not only is there often a complete change of the vortex pattern, but also the whole colour scheme alters. Fig. 32, Plate VII, shows, in monochrome, a particularly obvious response to sound.<sup>1</sup>

Sir James Dewar<sup>2</sup> used a similar arrangement to show the paramagnetism of oxygen in a very elegant manner. Fig. 33, Plate X, shows the experimental arrangements. A stream of oxygen from a drawn-out glass jet passes between the poles of an electro-magnet and impinges on a small soap film on the end of a glass tube. The characteristic double vortex is formed. When the magnet is excited the oxygen stream is deflected with a correspondingly magnified movement of the vortex pattern across the film.

### *Critical Fall*

These experiments of Sir James Dewar's<sup>3</sup> on vertical films stimulated in various ways led to the appearance of a very peculiar type of development with increasing

<sup>1</sup> *Proc. Roy. Inst.*, **24** (1), 234 [1923]; *Collected Papers*, **2**, 1364.

<sup>2</sup> *Proc. Roy. Inst.*, **24** (1), 245 [1923]; *Collected Papers*, **2**, 1369.

<sup>3</sup> *Proc. Roy. Inst.*, **24** (1), 209 [1923]; *Collected Papers*, **2**, 1343.

frequency. Instead of the black spreading steadily over the film, black spots suddenly appear in large numbers, especially in the thicker parts of the film, in a manner which suggests a partial breakdown of the structure. These small black spots rise to the top of the film and there coalesce to what is apparently a normal black film. This tumultuous development was called the "critical black fall," just as the normal extension of the black has been called the black fall, meaning, of course, the fall of the boundary between the black and coloured part of the film.

The critical fall is certainly to be regarded as abnormal, both on account of its rarity and the need for definite stimulation to bring the film into this unstable state.

Critical falls took place most frequently in films made from ammonium oleate solution, though they were also observed with tri-ethylamine and sodium oleates.<sup>1</sup> The critical fall occurs most regularly in solutions made from freshly and highly purified oleic acid.

The normal course of thinning is only followed as far as the production of colour, usually of fairly high orders. Then, in place of the usual further regular thinning and steady invasion of the whole film by the black, black spots suddenly appear in the thicker parts of the film through which they rise by tortuous paths until the whole is a writhing conglomeration of black and coloured discs. The whole of this abnormal development is over in a few minutes or even seconds, and the film settles down again as quickly as the disturbance has

<sup>1</sup> It should be remembered that almost all soap solution made from sodium oleate has some ammonia added. It is added because it has a marked effect in improving the solution for preparing films and bubbles; nevertheless, its presence is usually ignored. A single drop of strong ammonia is capable of neutralising no less than a quarter of a gram of fatty acid.

PLATE VIII.



FIG. 34.—Critical fall—thick viscous film.

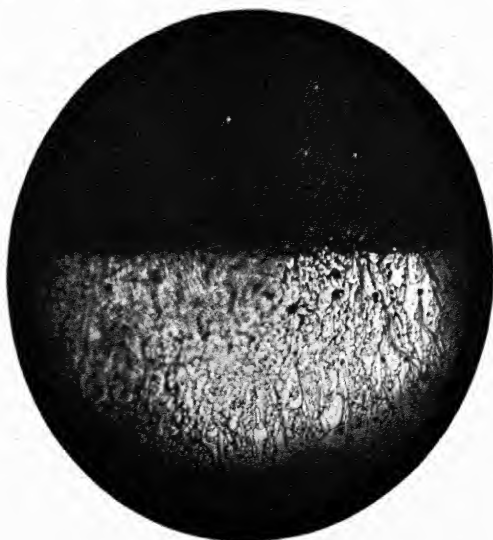


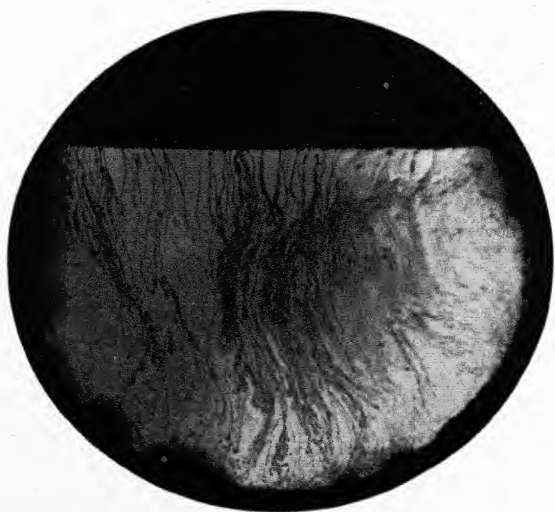
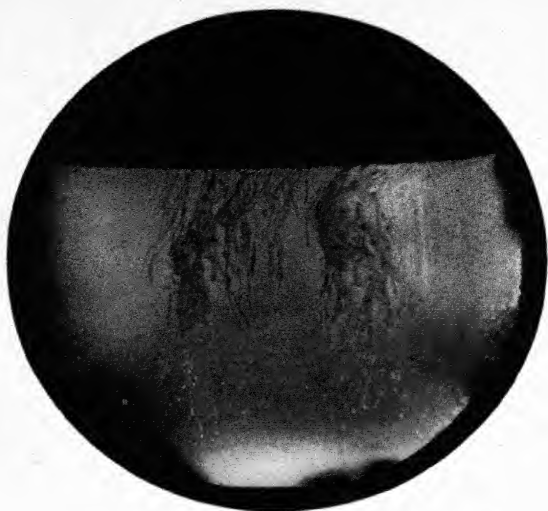
FIG. 35.—Critical fall in more dilute film.







PLATE IX.



FIGS. 36 and 37.—Early stages of slow critical fall.

arisen. By this time the film is about three-quarters black and the remainder very thick, only showing faint high-order colours or none at all. The actual extent of blackening brought about by a critical fall depends on the amount of liquid accumulated at the bottom of the film and, where adequate drainage is provided, may be as much as 90 per cent.

The appearance of a film during the critical fall depends on the thickness of the film at the start, on the rate of production of the black spots, and on the rate at which they rise through the coloured part to coalesce at the top, this last factor depending on the viscosity of the solution.

The appearance of this type of development of a film is extraordinarily impressive; no two critical falls are the same, but some idea of the nature and variety of the affair can be formed from photographs.

Fig. 34, Plate VIII, shows a typical critical fall in a thick film of high viscosity. The distribution of the colour bands shows the film to be quite thick, and, at the bottom, the black is clearly seen forming in a film at least three hundred times as thick as itself. Fig. 35, Plate VIII, shows a vigorous fall with a less viscous solution. The appearance of the earlier stages is of some interest; the critical development always starts from a point, usually in the thickest part of the film. For example, on one occasion a film was not lifted completely out of the soap solution; the critical fall started at the junction of the film and the liquid surface. This is, of course, the point of greatest curvature and hence of greatest activity of the Gibbs' ring which, in this case, consists of the whole solution. Figs. 36 and 37, Plate IX, show an early and a slightly later stage of a slow critical development.

It was found that the violence of the critical fall was augmented by increasing the illumination. In fact, finally using extremely pure soap solutions and a powerful arc, complete experimental control was gained over this peculiar form of development. Nevertheless, this observation does not throw much light on the origin and nature of the process, since it can, and in bubbles frequently does, occur in the absence of any strong illumination.

It was found that a film which was thinning normally could be made to give a critical fall by judicious application of an air jet. In such cases the fall did not start until the air current was cut off; it then proceeded with remarkable violence. In one such case a film of dilute solution was stirred up until, when the air supply was stopped and the vortex motion had settled down, the film was one-third black and the remainder brilliantly coloured. Suddenly the colour vanished, and only on close examination could it be seen that the lower part of the film was a seething mass of black and coloured discs, none of which was more than a millimetre in diameter.

Some light is thrown on the origin of the critical fall by its appearance in bubbles. Some abnormal black fall/time curves have already been given (Fig. 27, p. 49); in some of these a critical fall was observed to occur, whilst in the others it can only be assumed to have taken place from the form of the curves.

When a bubble is first blown, there is no equilibrium of tension of ammonia (and sometimes water also) of the bubble, the air inside it, the air surrounding it, and the solution at the bottom of the container. This lack of equilibrium soon adjusts itself, but occasionally a critical fall intervenes.

For example, a number of bubbles were blown from a

very pure newly prepared solution of 5 per cent. ammonium oleate in 50 per cent. glycerine. The first did not thin at all in 30 hours; a new one was therefore blown. A critical fall occurred 11 minutes after the first appearance of black at the top of the bubble. The second one, which was much thinner, being coloured gold and blue of the first order, required 12 minutes. The third, a similar one, took 25. This bubble was contracted by blowing air into the container and then re-expanded. A critical fall took place at once. Five cubic centimetres of ammonia were then introduced into the vessel. Critical falls were much more violent than before, and in some cases started before the bubbles were completely expanded (to about 16 cm. diameter).

Attempts to reproduce the critical fall in bubbles of sodium oleate made from the same oleic acid failed even when ammonia was added either to the solution or introduced into the container.

It appears that the critical fall is brought about either by loss of ammonia from the film or by the consequent re-absorption. A further complication is introduced by the occurrence of a critical fall in circumstances which point to the responsibility of water vapour. A large bubble, 37 cm. diameter, was blown in the large globe into which half a litre of pure water was then introduced. On the fourth day of its life it had become silvery white, but only a small collar of black had formed round the nozzle; a critical fall, consisting of the formation of huge black blobs, then followed until the bubble was about 60 per cent. black. This took about 45 minutes. No further extension of the black took place, and the bubble burst on the seventh day.

*Stratified Films*

Perrin,<sup>1</sup> while studying the behaviour of fluorescent substances, made the surprising discovery that addition of these dyes to a soap solution causes an entirely new development of films made from it.

He used aqueous solutions of potassium oleate up to a concentration of 10 per cent. and containing 10 per cent. or even more fluorescein. Films prepared from this solution were examined microscopically by reflected light.

The film thins normally until the usual interference colours appear; then, in Perrin's words, "il semble que la lame frissonne." The film is now seen to be composed of innumerable flakes (plages) of different tint but each one uniformly coloured and therefore of uniform thickness. The normal sequence of increasing thickness is entirely lost. Perrin's description of the progress of stratification may be amplified. The first sign of stratification is the appearance, usually in the middle of the field, of a more or less circular flake of colour clearly differentiated from the surrounding film; it rapidly grows in area; other flakes of various thickness and colour form around it. By this time stratification has started at a number of other points. The growing islands of parti-coloured stratification lurch about the film, growing irregularly in size as additional flakes spring slowly rather than grow into place, until the whole film is in this peculiar condition. A microphotograph ( $\times 100$ ), taken on a Lumière autochrome plate, of a film at this stage is shown in the frontispiece.

<sup>1</sup> *Annales de Physique*, (9), 10, 165 [1918], and P. V. Wells, *loc. cit.*, (9), 16, 79 [1921].

The process is clearly akin to crystallisation.<sup>1</sup> The stratified film is formed of a component whose amount is only a fraction of the total solution originally comprising the film. Around the edge, formed from the neighbourhood of the thick Gibbs' ring, are always found a number of flakes of high orders of colour. In a vertical film it is rare for the stratifications to be thicker than the rather dingy yellows and blues of the first order. More brilliant effects can be obtained by surrounding the developing film with filter-paper saturated with soap solution. In this way thicker stratifications can be produced as desired; the carmine and green stages being especially brilliant. Peculiarly striking, too, are the yellows and oranges of the second order, these colours never being seen to advantage in an ordinary soap film.

Stratification is accompanied by the expression of a large amount of liquid; "in the form of globules easily 20 to 50 microns in diameter" (Perrin); this is all occurring in a field of a millimetre or two.

Perrin found that stratification was started by the light used to illuminate the film, which is, of necessity, concentrated at a point. The film outside the field of illumination remained unstratified until exposed to light. Once any part of the film had become stratified it remained so. He made the further observation that only the light capable of exciting the fluorescence of the particular dye present was capable of starting stratification. This was shown by interposing a cell of the dye solution in the illuminating beam; in this way a cell of eosin solution, but not one of any

<sup>1</sup> Stratification is frequently observed to start from a nucleus whose form is not clear owing to the similarity of its refractive index with that of the soap solution. The existence of such a nucleus is clearly visible in Fig. 39.

other dye, protected a film containing eosin from stratification.

Several curious points arose in a repetition of this work by the writer. The solution used contained 5 per cent. potassium oleate and 10 per cent. of uranin (the sodium salt of fluorescein). When this was made from pure oleic acid no coloured stratifications could be obtained; addition, however, of some stearate rectified this. A solution containing 4.75 per cent. potassium oleate, 0.25 per cent. potassium stearate, and 10 per cent. uranin gave magnificent stratifications.

It was found that films made from this solution can behave in two quite different ways. If it is slightly alkaline (a trace of ammonia can be added with advantage), stratification is readily effected with some measure of experimental control. If, however, the solution is slightly acid, only grey and black stratifications are formed. The remarkable microphotograph shown in Fig. 38, Plate X, illustrates this type of stratification. The first and second orders of black (originally observed by Newton), surrounded by grey stages of increasing thickness, are seen growing in a silvery-white film. The peculiar overlaying of the independent strata, to which Perrin has drawn attention, is well shown to the left of the blacks.

The photographs reproduced here were obtained with a large projection reflection microscope; the film was held in a vertical position and illuminated by a small arc, the light from which passed through a water cell about 8 in. long. Films were conveniently obtained by brushing soap solution over the centre hole of a stainless steel safety-razor blade.

Under these conditions stratification took place without the necessity of stimulation by light.<sup>1</sup> When the full

<sup>1</sup> Perrin found that stratification starts spontaneously at 50° C.

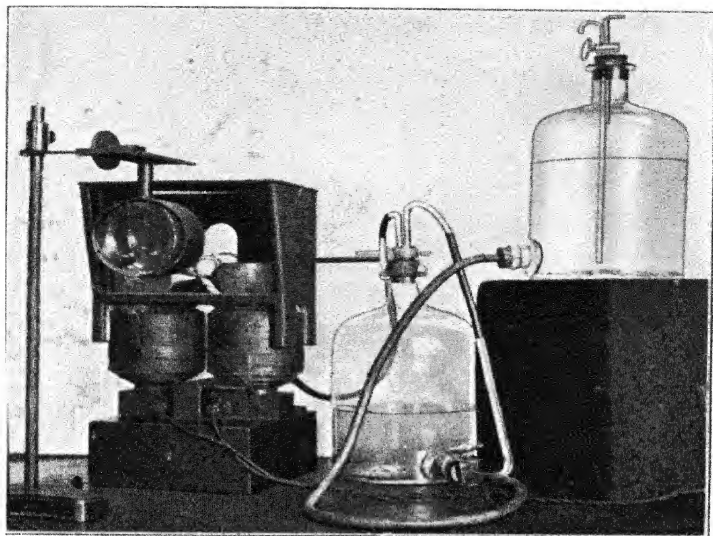


FIG. 33.—Experiment to show magnetic properties of gases.

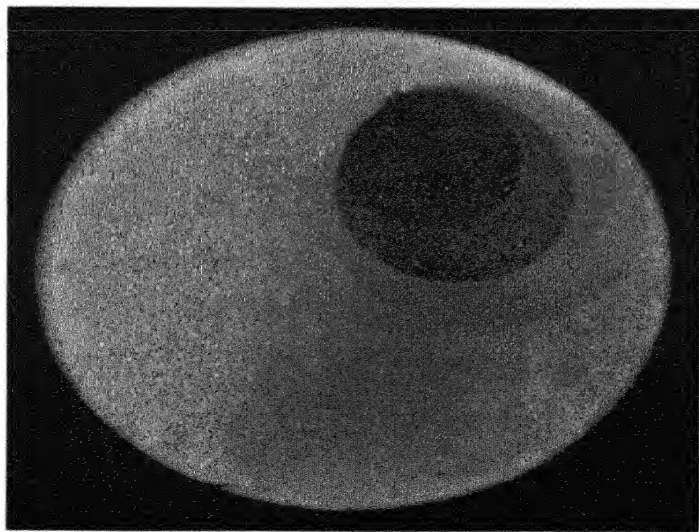


FIG. 38.—First and second orders of black surrounded by greys in stratified film.







PLATE XI.

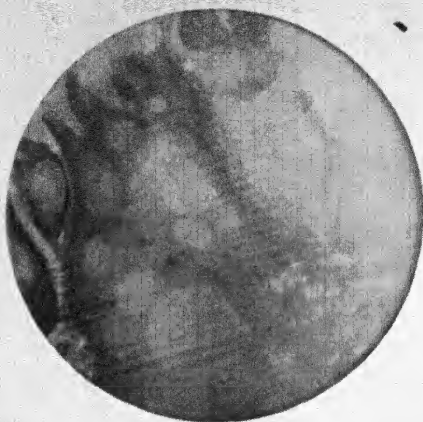


FIG. 39.

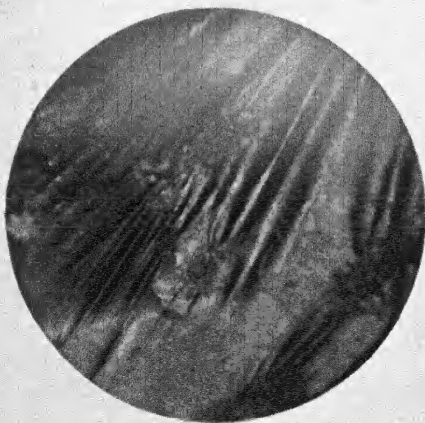


FIG. 40.

Solidification of stratified films.

illumination was turned on to the stratified film its whole character altered. The boundaries of the stratifications no longer remained arcs of circles but became jagged; a very limited amount of thinning took place, and finally the film crinkled in a way that showed it to be no longer liquid. Figs. 39 and 40, Plate XI, show early and late stages of this change.

If, under the conditions mentioned, the full illumination was turned on to the unstratified film it immediately set to a rigid conglomerate of indeterminate structure. To obtain a satisfactory photograph, the light was filtered through a concentrated solution of uranin while stratification and focussing were in progress; full illumination was then admitted and the exposure made at once.

It is clear, then, that stratification is an intermediate stage of a process which consists of the conversion of a liquid film into a solid one. The complete rigidity of the final crinkled film is shown by its form when it breaks. Frontispiece (B) shows such a film with a large hole in it.

## CHAPTER IV

### THE BLACK FILM

IN a film viewed by reflected light the thinnest stage appears black against the next thicker part, the silvery white, which reflects some 500 times as much light. The retardation of the internally reflected behind the directly reflected ray is so small in the black film that its thickness cannot be calculated accurately from the intensity. It is important that we should know what the actual thickness of the black is, whether it is a constant independent of the history of the film and how it compares with molecular dimensions.

The first and most systematic attempt to solve the first two questions is found in the work of Reinold and Rücker.<sup>1</sup>

These workers determined the thickness of the black film prepared from a number of different solutions. They calculated it from a comparison of the electrical conductivity of the film with that of the solution in bulk. As a check on this method, they measured the total thickness of a large number of black films by means of Jamin's interferometer.

They found the two methods give concordant results down to a thickness of 374  $\mu\mu$ . When the film is thinner than this the conductivity does not diminish in proportion to the thickness of the film, and the observed values of the conductivity of the black film are very much too large. They also made the rather curious observation

<sup>1</sup> *Phil. Trans.*, **172**, 447 [1881]; **174**, 645 [1883]; **177**, 627 [1886]; **177**, 679 [1886]; **184**, 505 [1893]; **184**, 627 [1893]. *Journ. Chem. Soc.*, **53**, 222 [1888].

that disturbance of the super-conducting black film reduces its conductivity towards the calculated value.

More recently, Hagenbach and Rickenbacher<sup>1</sup> have repeated this work and also find that the electrical method gives abnormal values for the thickness below 300  $\mu\mu$ .

Reinold and Rücker found, however, that addition of potassium nitrate to their soap solution prevented this increase of conductivity, so that the thickness of a film containing potassium nitrate could be measured accurately by this method. The following table shows the effect of various amounts of potassium nitrate added to a solution of one part of sodium oleate in 70 of water, the thicknesses given being those of the black film which was constant for any given solution.

Per cent. nitre.	Thickness of black film (calculated from conductivity).
3.0	10.6 $\mu\mu$
2.0	12.7
1.0	24.4
0.5	26.5
0.00	148.0 mean (max. 215, min. 79)

These figures show the abnormality of solutions containing no added electrolyte. A film 215  $\mu\mu$  thick would be blue-violet coloured, and not black at all. Not only are the figures abnormally large but they are hopelessly erratic.

They found a mean value of the thickness of the black obtained from solutions containing varying amounts of nitre by measuring the total thickness of some 50 films

<sup>1</sup> *Archives des Sciences*, **35**, 329 [1913]; **40**, 329 [1915].

optically. These results show that there is a real decrease of the thickness due to the nitre.

Per cent. nitre.	Thickness of black film (optically).
8.66	9.5 $\mu\mu$
5.2	11.1
3.0	10.7
0.9	24.7

The effect of glycerine is small.

Solution.	Thickness.	
	Optically.	Electrically.
Liquide glycerique .	10.7 $\mu\mu$	11.9 $\mu\mu$
Soap solution . .	12.2	12.5

They also found that the thickness of the black varies with the strength of the solution from which it is formed.

Solution.	Thickness (optical).
1 part sodium oleate in 30 of water . .	21.6 $\mu\mu$
"      "      " 40      "      "      "	22.1
"      "      " 60      "      "      "	27.7
"      "      " 80      "      "      "	29.3

While one part of soap in 40 and one in 60 of Plateau's liquide glycerique gave blacks 24.0 and 29.8  $\mu\mu$  thick

respectively. Working with a solution of 1.4 per cent. sodium oleate and 2.8 per cent. potassium nitrate, they find that the black film has a constant thickness of  $12.1 \mu\mu$ . They also obtained indications of the existence of another stage of black of about half this thickness.

Hagenbach and Rickenbacher measured the conductivity of a film rotated in its own plane and calculated the thickness to be  $14.3 \mu\mu$ . They found no difference in the thickness of the black prepared from solutions containing different concentrations of soap. They agree with Reinold and Rücker in placing the thickness of the black obtained from solutions of soap and water only at a much higher figure than the value for films containing nitre. Their main results are:—

Aqueous soap solution	.	.	.	.	.	41.6 $\mu\mu$
" " "	+3%	potassium nitrate	.	.	.	12.9
" " "	+20%	glycerine	.	.	.	22.8
" " "	+10%	glycerine+3% $\text{KNO}_3$	{			
			13.3 (2nd order)			
			7.3 (1st order).			

Johonnott<sup>1</sup> measured the thickness of the black film by two methods. Firstly, by determination of the mean value from the total thickness of a number of films measured by a Michaelson interferometer; and secondly, by a comparison of the intensity of the reflected light with that from a standard source controlled by passing through a pair of Nicol prisms, one of which could be rotated through a measured angle (see p. 69).

He concluded that the limiting thickness is independent of the concentration of soap, but that it is reduced by rise of temperature. He measured two clearly differentiated orders of black, one of which is twice the thickness of the other. He concludes that the thickness of the black is not constant, as it varies from 6 to  $40 \mu\mu$

<sup>1</sup> *Phil. Mag.*, (5), **47**, 501 [1899]; (6), **11**, 751 [1906].



in different solutions containing 1 to 2.5 per cent. of sodium oleate. The thicknesses of the first and second orders of black are 6 and 12  $\mu\mu$ . Solutions containing nitre or glycerine only form the thicker one. The three additional thicker blacks (p. 50) were too ephemeral for him to measure.

Johonnott made no allowance for the refractive index of his solution. With this correction his results for the thickness of the first and second orders of black are 5.7 and 11.4  $\mu\mu$ .

Perrin's discovery of the stratified film has led in his hands to an entirely new method of measuring the thickness of the black.<sup>1</sup> The appearance of a stratified film leads one irresistibly to the conclusion that the stratifications are formed according to some regular rule, and he suggested:

1. That, in a stratified film, the thickness of each layer is an integral multiple of an elementary thickness (which is of the order of 5  $\mu\mu$ ).
2. That the layers of a stratified film are formed by superposition of identical elementary leaflets in suitable number.

It follows, therefore, that the first-order black is probably the elementary leaflet. Extensive and careful determinations of the thickness of these stratifications have completely confirmed his conclusions.

Perrin's first method consisted of counting the maximum number of stratifications between the black and a stage whose thickness was known optically. This fiduciary point was provided by the violet stage which comes at the end of the first order of Newton's scale. By a peculiar chance this colour persists over a very small thickness

<sup>1</sup> *Loc. cit.*, p. 58.

gradient only; consequently, the thickness of the violet stratification must be very close to the optically calculated value, which is  $210 \mu\mu$  (for water).<sup>1</sup> In a number of films he counted:

- 18 to 19 stages of black, grey, and white;
- 17 to 18 stages of yellow, orange, and red; and
- 1 stage of violet.

The mean thickness per stratification is therefore  $5.7 \mu\mu$ .

The peculiar position of the violet stage is shown by the fact that he counted no less than 15 stages of different tint in the blue band which follows the violet.

Since the stratifications are not arranged in continuous order of increasing thickness, and, indeed, all stages are not represented in any one film, it is difficult to be certain that this enumeration is complete. Further, this method gives no direct information as to whether the increase of thickness per stage is constant. His second method throws some light on this point.

He counted the number of stages between the dark and bright bands produced by monochromatic illumination. We have seen that the condition for interference is that  $\theta = \frac{n\lambda}{4}$ , reinforcement taking place for odd values of  $n$  and extinction for even. The difference of thickness between a dark and bright band is therefore one-quarter of a wave-length.

Using a screen of turquoise blue which transmitted light of wave-length  $368 \mu\mu$  (in water), he counted from the black up to the first stratification of maximum brilliance 17 stages of intermediate tints; and from here to the second <sup>2</sup> minimum another 17. With a greenish-

<sup>1</sup> Reinold and Rucker's observed value is 230.

<sup>2</sup> Calling zero thickness the first.

yellow screen transmitting light of wave-length  $430 \mu\mu$  (in water), he was able to detect 40 stages up to and including the second<sup>1</sup> minimum. Between the second minima of these two screens he counted 5 stages, excluding the two extremes.

These results mean that 17 layers are required to build up a thickness of  $92 \mu\mu$ ; another 17 to increase it to 184, and 6 more to bring it up to 215. The thickness per layer for films of various thickness is therefore:

Thickness of film.	Mean thickness per layer.
0 to $92 \mu\mu$	$5.4 \mu\mu$
$92 \mu\mu$ to 184	$5.4$
$184 \mu\mu$ to 215	$5.3$
0 to 215	$5.4$

We have no reason to assume that values of the maxima and minima satisfying the equation  $\theta = \frac{n\lambda}{4}$  are exactly the thicknesses of the corresponding layers. In a continuous film there must be a point where the thickness is exactly equal to  $\frac{n\lambda}{4}$ . A stratified film is not continuous, and the brightest (or darkest) stratification is merely the nearest to the thickness  $\frac{n\lambda}{4}$ . Suppose this thickness to fall just half-way between the actual thicknesses of two adjacent stratifications, so that

$$\frac{n\lambda}{4} = N\theta_1 + \frac{\theta_1}{2} = (N + 1)\theta_1 - \frac{\theta_1}{2},$$

where  $\theta_1$  is the thickness per layer and  $N$  the appropriate number of layers. In this case the two stratifications

<sup>1</sup> Calling zero thickness the first.

would appear to be of equal tint and the assumption that  $\frac{n\lambda}{4} = N\theta_1$  would be incorrect by  $\frac{\theta_1}{2}$ . Clearly there is the possibility of this error at every maximum and minimum except the first minimum of zero thickness. Counting from zero the maximum possible error in the deduced thickness per layer is one  $2N^{\text{th}}$  part of its value,  $N$  being the number of stages used in the estimate.

After correcting for the difference of the refractive index of the soap solution from that of water, he arrives at a value of  $5.2 \mu\mu$ .

This work was further extended and confirmed by P. V. Wells.<sup>1</sup> He employed two methods. In the first, a beam of light is divided into two parts, one being reflected from a stratified film and the other passing through a pair of Nicol prisms. The two halves are brought together again as the two halves of the field of a microscope in which they are viewed through a monochromatic screen. One of the Nicols is rotated until the two halves of the field are equally bright. The angle through which it is rotated gives, by a simple calculation, the required intensity.

The intensity of the incident light,  $I$ , reflected  $I_0$  from a film is given by the equation

$$\frac{I}{I_0} = K \sin^2 \frac{\pi \Delta}{\lambda} \quad . \quad . \quad . \quad (9)$$

where  $\Delta$  is the retardation of the internally reflected ray. And the intensity of the light passing through the Nicols by the equation

$$\frac{I}{I_0} = \cos^2 a_n \quad . \quad . \quad . \quad (10)$$

where  $a_n$  is the rotation of one of them.

<sup>1</sup> *Loc. cit.*, p. 58.

He allows for the effect of stray light, and finally obtains the following equation:—

$$\sin^2 \frac{\pi \Delta}{\lambda} = \frac{\sin^2 a - \sin^2 a_0}{\sin^2 a_m - \sin^2 a_0} \quad . \quad . \quad (11)$$

where  $a_m$  is the complement of the angle between the principal planes of the Nicols for equality of the two halves of the field when the film under observation has the thickness such that  $\Delta = \frac{\lambda}{2}$ , that is, the first bright band;  $a$  the observation of the film being measured and  $a_0$  the observation with no film.  $\Delta$  can therefore be obtained by observation of three angles, and the result so calculated is independent of the presence of stray light in the field.

Now for light at normal incidence,

$$\Delta = 2\mu\theta \quad . \quad . \quad . \quad (12)$$

but here we have it concentrated on the film and he uses the formula

$$\Delta = 2\theta\sqrt{\mu^2 - \frac{1}{2}\sin^2 a} \quad . \quad . \quad (13)$$

where  $a$  is the size of the aperture of the objective in front of the film. Combining these he gets the following equation:—

$$\sin^2 \phi = \frac{\sin(a + a_0) \sin(a - a_0)}{\sin(a_m + a_0) \sin(a_m - a_0)} \quad . \quad (14)$$

and, from this, the thickness  $\theta = 1.14\phi \times 10^{-7}$ .

According to Perrin, the thickness of any layer,  $\theta_n$ , is  $n$  times the thickness of the elementary leaflet,  $\theta_1$ , which is about  $5 \mu\mu$ . The method outlined above provides a large number of numerical data for the thicknesses of various values, all unknown, of  $n$ . The elementary thickness,  $\theta_1$ , is the largest common divisor of the thicknesses of all the possible stages, to some of which the observed

values are approximations. A trial value is found for  $\theta_1$  and the integral values of  $n$  from the value of  $\frac{\theta_n}{\theta_1}$ . The values of  $\theta_1$  cannot vary by more than  $\frac{\theta_1}{n}$  with this method of calculation. The differences  $\left(\frac{\theta}{\theta_1} - n\right)$  are the deviations from the "law of multiple thicknesses"; though they cannot be trusted for large values of  $n$ .

The results so obtained for the first three orders of black are shown in Table VI.

TABLE VI.

Thickness measured ( $\theta n$ ).	Order of stratification ( $n$ ).	$\frac{\theta n}{n}$ .	$\left(\frac{\theta n}{\theta_1} - n\right)$ .
4.3 $\mu\mu$	1	4.3 $\mu\mu$	0.09 $\mu\mu$
4.8	1	4.8	0.01
4.9	1	4.9	0.03
3.9	1	3.9	0.13
4.6	1	4.6	0.02
4.8	1	4.8	0.07
•		Mean 4.55	
8.3	2	4.15	0.14
8.9	2	4.45	0.00
8.6	2	4.3	0.09
9.1	2	4.55	0.02
		Mean 4.36	
13.8	3	4.6	0.10
13.7	3	4.57	0.04
		Mean 4.59	

The complete results up to the seventeenth order of stratification are shown graphically in Fig. 41. Of course this is still a very thin film; nevertheless, the results are sufficient to establish the correctness of Perrin's postulates. This very careful work, however, contains fluctua-

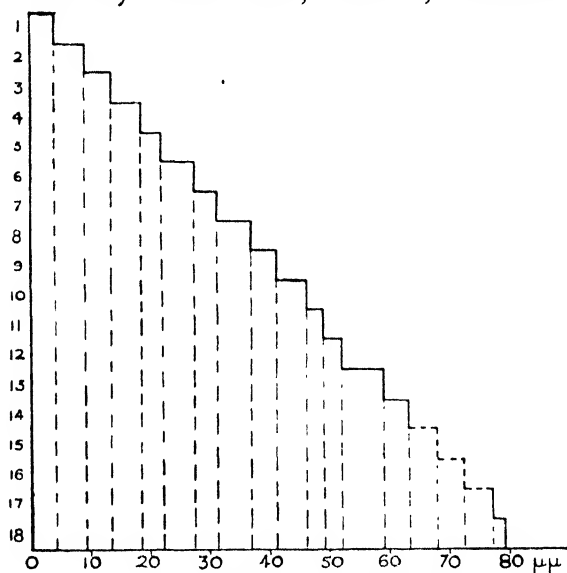


FIG. 41.—Thickness of stratified films.

tions of the value of  $\frac{d\theta}{dn}$  of such magnitude as to suggest that the elementary leaflet is not perfectly constant.

The same author used a second method to measure the thickness of coloured stratifications. The optical arrangement is similar, except that the colour of the stratification to be measured is compared with that produced in the comparison field by a quartz wedge, the arrangement being that of Levy's comparator. We have seen that the retardation of the internally behind the directly reflected ray is  $2\mu\theta$ . Here we have

$$2\mu\theta = a\chi + b \quad . \quad . \quad . \quad (15)$$

where  $\chi$  is the displacement of the wedge and  $a$  and  $b$  are constants. For a small alteration of thickness  $d\theta$  we have

$$d\Delta = 2\mu d\theta = a d\chi \quad . \quad . \quad (16)$$

The constant  $a$  is obtained by measuring the minima corresponding to  $\Delta = \lambda$  and  $\Delta = 2\lambda$  for known values of  $\lambda$ .

In this way he measured the thickness of a number of stratifications, starting from the purple at the end of the first order whose thickness, as we have seen, is known accurately. Over a range of the seven neighbouring colours he obtains the mean value of 4.17 for  $\theta_1$ . From eight stages of the second order of coloration he gets 4.34  $\mu\mu$ .

He finally adopts the value of 4.4  $\mu\mu$  for the thickness of the elementary leaflet. This, when corrected for the refractive index of the soap solution, becomes 4.2  $\mu\mu$ .

He also carried out measurements of films made from other solutions:

1. 5 per cent. potassium oleate in water.
2. 5 per cent. potassium oleate, 15 per cent. uranin, and 60 per cent. glycerine.
3. 5 per cent. potassium oleate, 15 per cent. uranin, 25 per cent. sugar, and 55 per cent. glycerine.
4. 4 per cent. potassium oleate, 15 per cent. uranin, and 75 per cent. glycerine.

The results are:

Solution.	Photometric method.	Colorimetric method.
1	4.42 $\mu\mu$	.. $\mu\mu$
2	4.50	3.92
3	4.47	..
4	4.00	3.2



He suggests that the thickness of the elementary leaflet is constant for all solutions. His figures are not directly comparable, as no correction is made for the difference of refractive index which certainly exists.

*The Passage of Gases Through the Black Film*<sup>1</sup>

As a result of their extreme tenuity black films are porous. We have already seen that this property sets a limit to the "life" of a black bubble. The air inside it is forced out by the internal excess pressure.

Now there is a simple relation between the rate of diminution of the diameter and the rate of effusion of air. If  $V$  is the volume of the bubble and  $A$  its area, then

$$V = \frac{\pi}{6}D^3$$

and

$$A = \pi D^2,$$

so that

$$dV = \frac{\pi}{2}D^2dD,$$

which can be written

$$\frac{1}{2}AdD.$$

The rate of gas effusion per unit surface  $\frac{dV}{A}/dT$  is therefore

$$\frac{1}{2}\frac{dD}{dT} \cdot \cdot \cdot \cdot (17)$$

The rate of gas effusion is proportional to the internal excess pressure, which is, as we have seen,  $\frac{8\sigma}{D}$ . The rate of diminution of the diameter is therefore inversely pro-

<sup>1</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **22** (1), 192 [1917]; *Collected Papers*, **2**, 1187 and 1230.



PLATE XII.

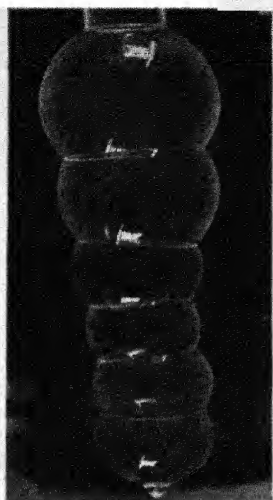


FIG. 44A.

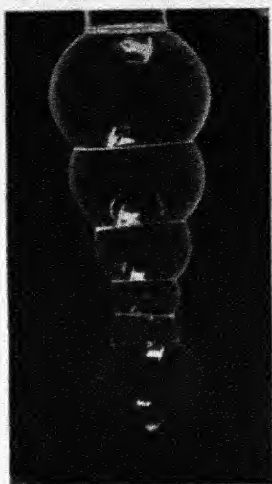
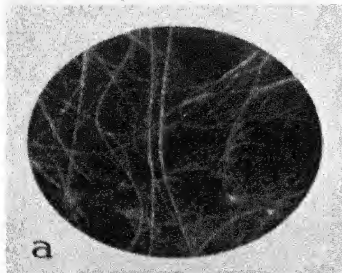
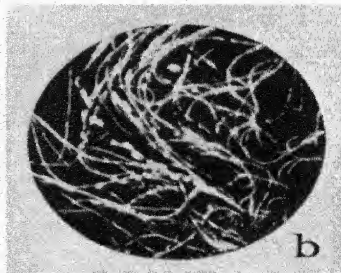


FIG. 44B.

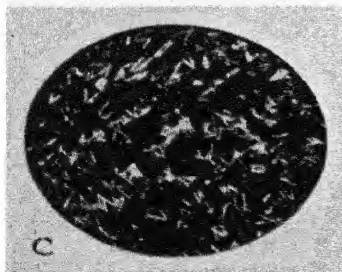
Rate of contraction of segments of a bubble chain.



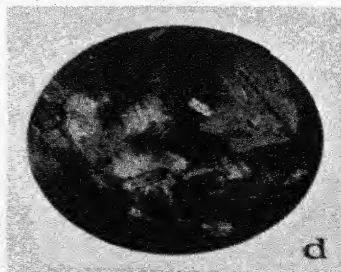
a



b



c



d

FIG. 47. Ultramicrophotographs of soap coagels.

portional to itself, and the diameter/time contraction curve is a parabola. This has been verified experimentally for a bubble in hydrogen. The curve is shown in Fig. 42.<sup>1</sup> The rate of effusion of air is so much slower that complete contraction curves cannot be obtained. Fig. 43 shows the earlier stages of the contraction of a 33-cm. bubble which was measured with extreme accuracy. The rate of diminution of diameter, and hence of gas effusion, shows the expected increase as the diameter

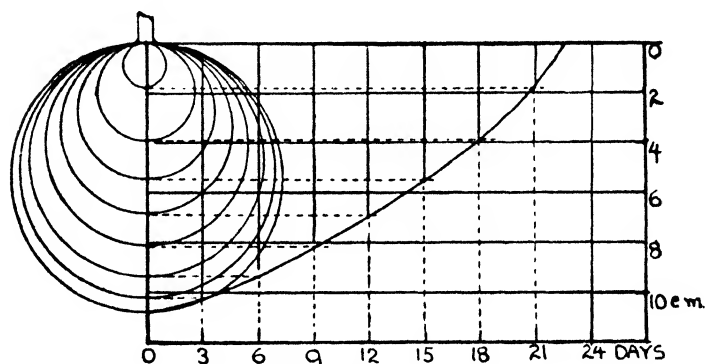


FIG. 42.

itself becomes smaller, although it is too small to detect in the curve. The rate for the last fifty days is 0.032 c.c./cm.<sup>2</sup>/day as compared with 0.030 from the tenth to the sixtieth.

Fig. 44, Plate XII, shows the greater contraction rate of the smaller segments of a bubble chain over a period of 9 days. The rate of gas effusion can be measured more easily in small bubbles, and the rates so obtained provide an interesting means of comparison of black films obtained from different sources. Table VII shows some tentative measurements which illustrate this point;  $R$  is the ob-

<sup>1</sup> *Loc. cit.*, p. 74.

served rate of gas transference in cc./cm.<sup>2</sup>/day, while  $R_1$  is the rate calculated for a bubble 1 cm. diameter. The

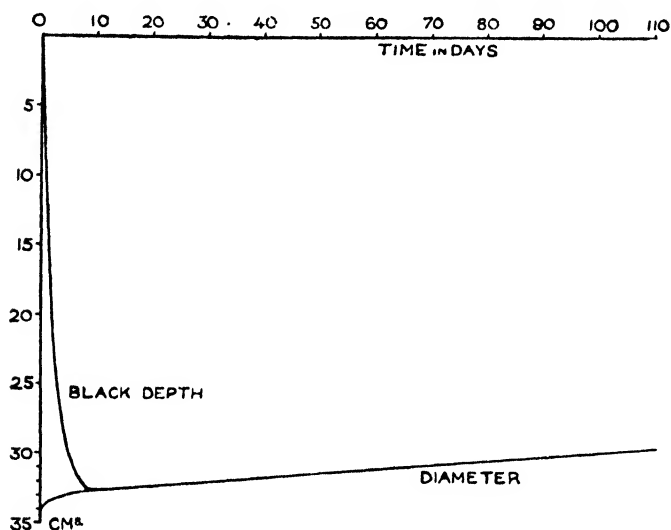


FIG. 43.—Contraction of large black bubble.

third set of results refers to  $3\frac{1}{3}$  per cent. soap in 33 per cent. glycerine solution, while the others are for 5 in 50.

TABLE VII.

	<i>Air.</i>		<i>Hydrogen.</i>			
Diameter.	$R$ .	$R_1$ .	$R$ .	$R_1$ .	$R$ .	$R_1$ .
cm.						
4	..	..	0.22	0.88	0.31	1.24
6	0.065	0.39	0.14	0.84	0.25	1.5
7	0.035	0.25	..	..	..	..
8	0.030	0.24	0.10	0.80	0.20	1.6
10	..	..	0.053	0.53	0.17	1.7

Definite statements cannot be made from such results,

but experience of a large number of contraction rates suggests that the constitution of the black depends on the history of the film, which, of course, includes that of the solution from which it was prepared.

Sir James Dewar has also studied the effect of increasing and reducing the pressure. As we should expect, the former greatly reduces the rate of effusion<sup>1</sup> while the latter speeds it up so much that accurate measurements cannot be made with these ephemeral bubbles.<sup>2</sup>

We have already seen that the so-called plane film is in reality slightly convex. The result of this is that, when the film has drained to the black stage, the small pressure below the film due to its weight causes air transference through it, and it very slowly travels down the container. As we should expect, from the smallness of the curvature, the actual movements are very small, and in films more than a few centimetres in diameter, can only be detected over very long periods. Nevertheless, such movements are very important from the point of view of the stability of the film, since the liquid in the Gibbs' ring can only lubricate the downward passage for a short way. Of course, the smaller the Gibbs' ring is, the smaller the curvature and rate of fall. An idea of the time taken by films of various diameters to fall 1 cm. is given by the following figures:—

Diameter.				Time.
1.15 cm.	.	.	.	11 days.
2.86 „	.	.	.	74 „
9.0 „	.	.	.	220 „
19.0 „	.	.	.	several years.

<sup>1</sup> For 4- and 6-cm. hydrogen bubbles under 6.5 atmospheres  $R_1$  is .33 and .25.

<sup>2</sup> A 3-cm. air bubble at about 1 mm. pressure gave  $R_1 = 130$ .

Apart from this gas effusion, which results from the internal excess pressure, diffusion takes place at a much higher rate. It is easily measured by circulating the required gas on one side of a plane film in a calibrated cylindrical vessel. The movement of the film along the vessel shows the progress of the diffusion. When hydrogen is circulated on the one side with air on the other, a maximum diffusion rate of  $42 \text{ c.c./cm.}^2/\text{hour}$  was reached. With oxygen in place of air, the rate was  $50 \text{ c.c./cm.}^2/\text{hour}$ .

## CHAPTER V

### SOAP SOLUTIONS

#### *The Distribution of Solute*

EVIDENCE has already been given of the existence of a specific surface layer in solutions of surface-active substances such as soap (pp. 10 and 11).

Obviously, in a soap film such a difference of properties of surface and interior assumes the highest importance. Here the fraction of the total liquid in the surface layer, whatever its depth, is very much larger than is usually the case.

We have seen that the action of surface tension in any substance is to reduce the free surface energy *as far as possible*. As measured, surface tension is a cumulative effect balanced against other forces. Surface tension in action is due to individual molecules; surface is reduced by the attraction of molecules from the surface into the interior.

In the case of solutions we may expect another effect. If the solute lowers the surface tension, it will tend to collect at the surface until the maximum possible reduction is achieved. If, on the other hand, the solute raises the surface tension, then we should expect the surface layer to contain less than the bulk of the solution.

This difference of concentration of the surface and the interior of a solution is called "adsorption." When there is concentration of solute in the surface layer, as in the case of soap, it is said to be positive; the reverse case being called negative.

Several questions arise at once. How much solute is adsorbed to form the surface layer of minimum free



surface energy? Is adsorption complete in the sense that a layer of pure solute or of pure solvent is formed? How do the adsorbed molecules behave when they reach the surface? And finally, how do they affect the surface tension?

Willard Gibbs has given a theoretical answer to the first question on thermodynamical grounds.<sup>1</sup> He considers an isothermal dilution cycle of a solution containing a given mass of solute. If the volume is  $V$ , the surface tension  $\sigma$ , osmotic pressure  $P$ , and the superficial area  $A$ , then

$$\frac{d\sigma}{dV} = \frac{-dP}{dA} \quad . \quad . \quad . \quad (18)$$

That is, if the surface tension varies with the volume, and therefore the concentration, of the solution, then the osmotic pressure varies with its superficial area. Or, in other words, the concentration of the solution varies with its superficial area. This can only follow where there is a difference between the concentration of the surface and the bulk of the solution.

Now suppose that  $a$  is the number (positive or negative) of molecules adsorbed per unit area; then the total adsorption is  $Aa$ . If  $n$  is the total number of molecules in the solution, then the concentration  $C$  of the bulk of the solution will be

$$C = \frac{n - aA}{V}.$$

Substituting in equation 18 he gets

$$a = - C \frac{d\sigma}{dc} \bigg/ \frac{dP}{dc} \quad . \quad . \quad . \quad (19)$$

---

<sup>1</sup> *Collected Papers*, 1, 233 ; see also *Surface Tension and Surface Energy*, Willows and Hatschek, pp. 48 and 109.

Since osmotic pressure increases with concentration  $\frac{dP}{dc}$  is always positive. Equation 19 therefore means that positive adsorption takes place where the surface tension of a solution falls with increasing concentration and negative adsorption when it rises.

Before we consider the nature of the adsorption layer, it will be necessary to discuss the components of soap solutions and the properties of surface layers in general.

### *The Composition of Soap Solutions*

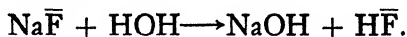
Solutions are usually regarded as perfectly homogeneous. In this book we are considering individual molecules, and on this scale it is clear that the assumption is not true. In colloidal solutions discontinuity appears on a scale much larger than molecular. In so-called molecularly disperse solutions we have further dissociation into ions, which are in turn associated in some way with solvent molecules. The peculiar position of the soaps is shown by the fact that they are present in aqueous solution as crystalloid and as colloid.

As a result of this, many of their physical properties are anomalous. Their aqueous solutions are cloudy; sometimes they are doubly refracting; their density is less than the mean of their constituents; their viscosity is large and subject to peculiar fluctuations; they cannot be made to boil regularly. As we have seen their surface tension is very small.

It has been pointed out that a soap solution consists of water and a long-chain compound which possesses a grouping at one end sufficient to render it soluble; the commonest substances of this sort being the alkali salts of the fatty acids.

It was formerly believed (and still is by most authors

of text-books) that soap is largely dissociated in aqueous solutions according to the equation:



The hydrolysed alkali was held responsible for the electrical conductivity, and it was also given the credit for their detergent action. It is now known that the actual amount of hydrolysed alkali is quite small and insufficient to account for the observed conductivity. The true mechanism of the detergent action of soap has already been described (p. 13).

This equation is, in fact, only true for very dilute solutions. The present state of our knowledge of the components of soap solutions is the result of the researches of McBain and his co-workers.<sup>1</sup>

In the first place the degree of hydrolysis was measured by means of a hydrogen electrode and the results so obtained were confirmed by a chemical method. The *OH* ion acts as a catalyst in the decomposition of nitroso-triacetonamine. From the rate of its decomposition, therefore, the degree of hydrolysis can be measured.

The osmotic pressure was then determined. This operation presents certain difficulties, as the usual boiling-point methods are inapplicable. A dew-point method was finally used. The soap solution was contained in a thermostat; above the surface and in the vapour from it, was suspended a polished silver vessel through which water at any required temperature was circulated. By previously dipping part of the silver vessel into boiling

<sup>1</sup> *Journ. Chem. Soc.*, **99**, 191 [1911]; **101**, 2042 [1912]; **105**, 417, 957 [1914]; **113**, 435, 825 [1918]; **115**, 1279, 1300 [1919]; **117**, 530, 1506 [1920]; **121**, 621, 711, 1101, 1320, 1360, 2161, 2325 [1922]; **123**, 2417 [1923]; 2679 [1927]. *Proc. Roy. Soc., A.*, **97**, 44 [1920]. *Journ. Phys. Chem.*, **23**, 673, [1924]. *Third Report of British Association on Colloid Chemistry* [1920], pp. 1-30.

water, a sharp boundary was caused to appear at the dew-point. By comparison with pure water the depression of vapour pressure could be determined at any temperature. These results were confirmed by freezing-point data.

Thirdly, the electrical conductivity was measured at the same temperature. Fig. 45 shows the results for the

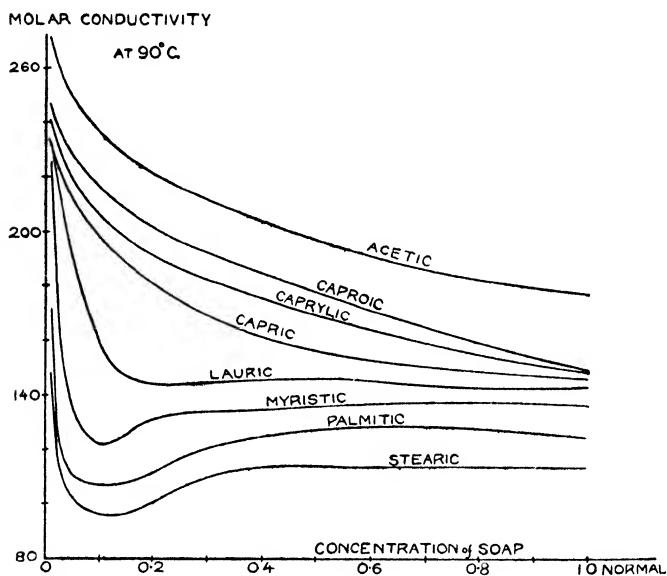


FIG. 45.—Electrical conductivity of potassium salts of fatty acids.

potassium salts of the normal saturated acids; it is obvious that the soaps, that is from lauric upwards, are abnormal.

Now it is found that the osmotic pressures of the soaps are only about half what we should expect from that of the acetates. If we assume that the whole of this effect is due to the sodium ions present, then the number so estimated is only sufficient to account for about half the observed electrical conductivity. McBain therefore

suggests that the remainder of the conductivity is due to electrically charged colloid aggregations, which, of course, exert no appreciable effect on the dew-point measurements. The remainder of the soap must also be present in colloidal aggregation, since it is exerting no osmotic pressure either.

The osmotic-pressure data, then, give a measure of the amount of alkali kation, fatty acid anion, and molecularly disperse neutral soap. If, in the conductivity results, we ignore the effect of the slowly migrating fatty anion we can calculate the amount of alkali, free and associated with the conducting colloid particles. This subtracted from the osmotic pressure figure gives the amount of fatty acid anion + molecularly disperse soap. The difference between this and the total amount of fatty acid present gives the amount of the latter present as neutral and conducting colloid. Obviously, the total number of fatty acid molecules present as ionised colloid is limited by the number of alkali kations.

On these lines McBain has been able to form a picture of the composition of soap solutions which is certainly very near to the true state of affairs. Table VIII gives the results for potassium oleate at room temperature.

TABLE VIII.—COMPONENTS OF POTASSIUM OLEATE SOLUTIONS  
AT 0-18° C.

Concentration. Mols./litre.	Neutral colloid.	Colloid ion.	Molecularly disperse soap.	Fatty anion.	Alkali kation.
0.1	0.05-0.08	0.02-0	0.02-0	0-0.02	0.02
0.2	0.14-0.15	0.05-0.04	0.01-0	0-0.01	0.05
0.4	0.28-0.29	0.11	0	0	0.11
0.5	0.35-0.36	0.14	0	0	0.14
0.6	0.41-0.43	0.17-0.16	0.01-0	0-0.01	0.17

Fig. 46 is constructed from McBain's results to show the proportion of colloidal constituents in solutions of the potassium salts of the acids of the acetic series at 90° C. The ordinates, up to the dotted curves, show the amount of colloid ion: and of neutral colloid from the

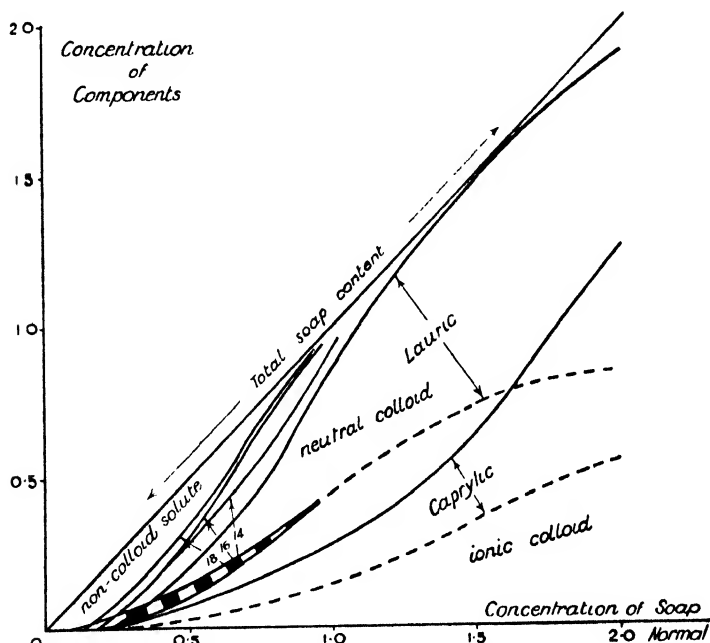


FIG. 46.—Components of soap solutions.

broken to the full curves; the full straight line giving the total concentration of solute. The smallness of the non-colloidally disperse salt, except at low concentrations and for the lower members, is clear. The curves labelled 18, 16, and 14 refer, of course, to these members of the homologous series—stearic, palmitic, and myristic.

*The Components of Soap Solutions*

It is obvious that the peculiar properties of the soaps are bound up with their colloidal constituents, that is the neutral micellæ and the ionic micellæ.<sup>1</sup> The former are responsible for much of the abnormality of the physical properties of soap solutions, and in consequence a considerable amount of information has accumulated concerning these particles.

It appears that they have one dimension very much larger than the other two; they are, in fact, threads. These extremely elongated particles are easily oriented by movement of the solution, which is thereby rendered doubly refracting. This double refraction is due to the cumulative optical activity of the individual anisotropic particles. Freundlich<sup>2</sup> describes a striking experiment to illustrate this property. Solution containing thread-like colloid particles flows through a tube of triangular section. Monochromatic light—he uses the hydrogen C line—is passed through this prism and is thereby divided into two, the ordinary and the extraordinary, which are, of course, polarised at right angles. Soap solutions frequently become streaky or develop a silvery opalescence when stirred. This is also a consequence of the thread-like form of the colloidal particles. Light is scattered at right angles to the long axis; solution in motion contains the particles oriented with this axis along the direction of flow. It therefore only appears bright when illuminated at right angles to the direction of flow and viewed along it.

The most direct evidence we possess of the thread-like

<sup>1</sup> The micella is the ultimate chemical colloidal unit.

<sup>2</sup> *Colloid and Capillary Chemistry*, English trans., pp. 408 and 409.

form of these particles is provided by ultramicroscopic examination of soap coagels.<sup>1</sup>

Hot aqueous soap solution is optically empty. We cannot set an upper limit to the size of the invisible particles which are certainly present, since the conditions for the visibility of a particle ultramicroscopically are too complicated. The intensity of light scattered is proportional to the square of the size of the particle, on the difference of refractive index of the two phases and on the intensity of the illumination.

As the solution cools, particles in Brownian motion appear; threads then form, the single ones being also in feeble Brownian motion. These particles increase in number and to some extent aggregate to irregular clusters.

The last stage, which is rarely complete and frequently does not take place at all, is the conversion of the fibrous form to lamellar crystals. McBain mentions a specimen of sodium palmitate which was only partially converted to the lamellar form in five years.<sup>2</sup>

These threads have a number of peculiar properties. They always appear at their full size, not growing like a crystal, but giving the impression of having been formed by aggregation of a number of similarly shaped amicronic particles. The threads are often curved in a remarkable manner, sometimes in perfect sine curves. Fig. 47A, Plate XII, shows the appearance of sodium laurate threads. This curvature is most marked in the lower members of the fatty acid series.

The nature of the base in the soap has a great effect on the form of the particles. Sodium soaps form very

<sup>1</sup> Zsigmondy and Bachmann, *Kolloid Zeitschr.*, **11**, 150 [1912]; Darke, McBain, and Salmon, *Proc. Roy. Soc., A.*, **98**, 395 [1921].

<sup>2</sup> *Loc. cit.*



long threads (Fig. 47B, sodium oleate); their length may be as much as 100  $\mu$ , while their thickness remains amicronic. Potassium soaps do not form these long threads; they usually form short ones which exist as twins with a characteristic V shape (Fig. 47c, potassium stearate). This lack of the extreme asymmetry of the sodium soaps no doubt accounts for the much greater readiness of the potassium soaps to change into the lamellar form. Fig. 47D shows the lamellar form of sodium laurate.

McBain suggests that the growth of these fibres is a result of surface-tension considerations rather than a crystallisation. For this reason the smallest particles are the most crystalline in appearance; the aggregations visible microscopically have no particular form at all.

Now the fatty acids exhibit a much greater range of properties than is usually recognised, and one in particular is much more definitely crystalline than any other. This is stearolic, an acid closely related to stearic and oleic; its chemical constitution has already been described (p. 19).

Aqueous solutions of the alkali salts of this acid are typical soap solutions, but on cooling a hot solution the soaps crystallise out in quite definite form. Microscopic examination of these forms provides an interesting extension of the ultramicroscopic results just described.<sup>1</sup> The cooling and crystallisation of solutions containing about 2 per cent. of soap was followed between crossed Nicols with a magnification of 50. Potassium stearolate is deposited in square plates (Fig. 48A, Plate XIII). In striking contrast to this is the sodium soap which forms a mass of very fine silky threads (Fig. 48B). On

<sup>1</sup> Microscopically, we see the actual particles; ultramicroscopically, we only see the light diffracted by particles themselves invisible. From the shape of this diffraction image we can infer the shape of the particles.

PLATE XIII.

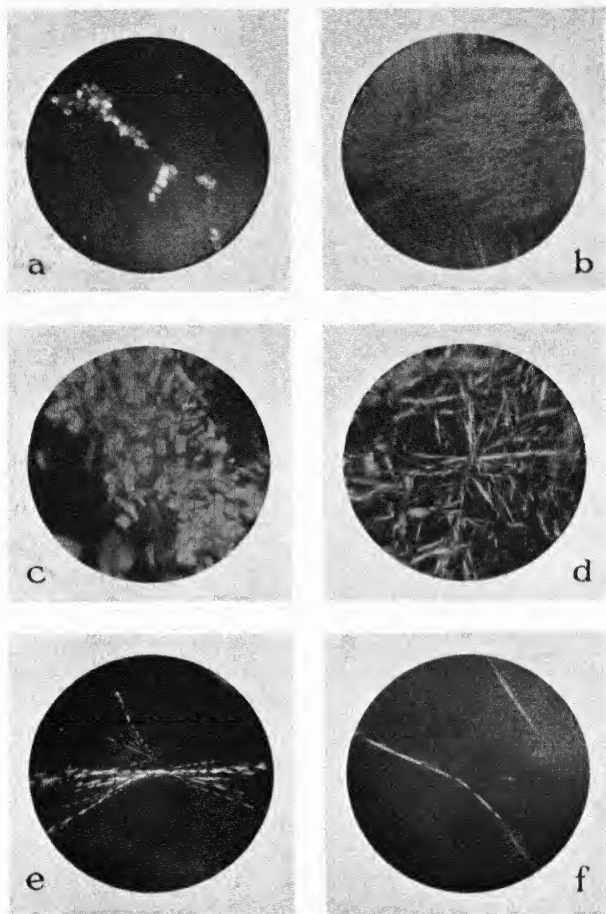


FIG. 48.—Microphotographs of stearolates.  $\times 50$ .





PLATE XIV.

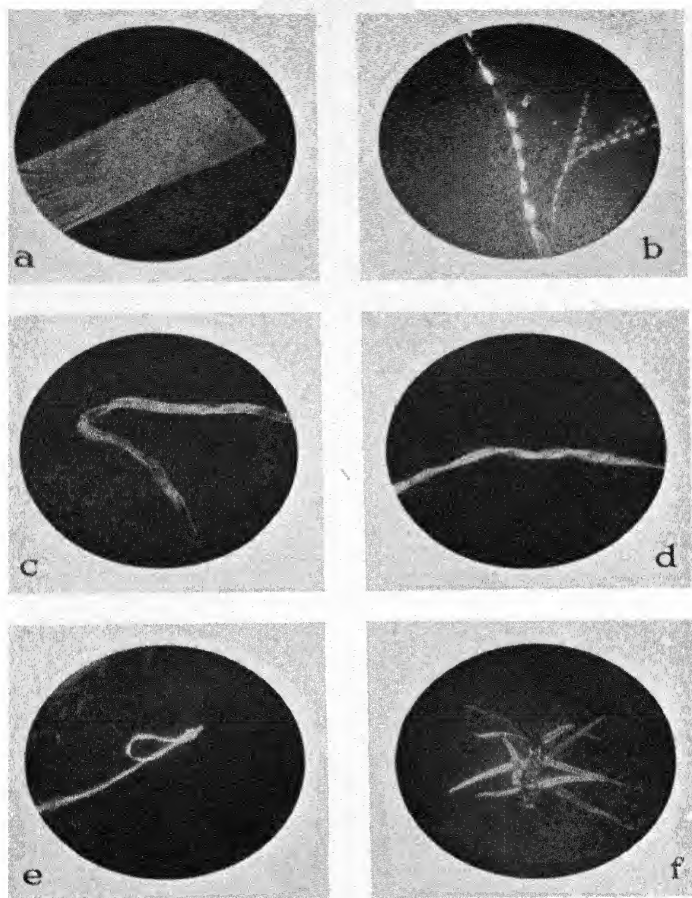


FIG. 49.—Microphotographs of stearolates.  $\times 50$ .

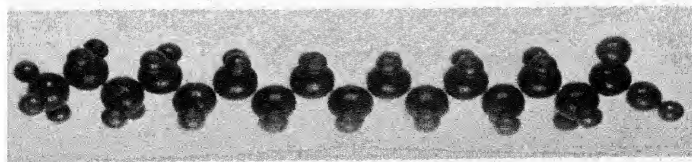


FIG. 50.—Model of palmitic acid molecule (Sir W. Bragg).  
 $\times 20,000,000$ .

one occasion the sodium soap separated from a newly prepared solution in rhombic plates, but this behaviour could not be reproduced. Most interesting is the ammonium soap; from strongly alkaline solution it crystallises in rhombic plates (Fig. 48c), the angle of which is not so acute as that of the sodium salt. If, however, the solution is neutral, or slightly acid, the soap is deposited in curious bundles of fibres (Fig. 48d and e). Dilute slightly alkaline solutions form long articulated crystals (Fig. 48f).

In addition to these crystals there are in every solution very curious large fibres. These are never seen to grow; they are always first seen in the field at full size; their outlines, however, sometimes become blurred as if by a growth of micronic whiskers.

It is possible to obtain all these forms on a large scale. If a trace of ammonia is added to a solution of the potassium soap, single crystals large enough to handle can be obtained although they are extremely thin. Fig. 49A, Plate XIV, shows the microscopic appearance of such a crystal; this particular one was brilliantly coloured by high-order interference colours—mainly carmine of the fourth order. Its stratified structure was perfectly clear and can still be recognised in the monochrome reproduction. Fig. 49B also contains a stratified crystal, one-half of which is thicker than the other. This photograph also shows a well-developed example of the fibres deposited from slightly acid ammonium stearolate solution. A similar structure has been recognised ultra-microscopically in sodium oleate coagels. Fig. 49B is apparently a very large specimen of this form; its appearance seems to be the result of a twisted ribbon structure. The long articulated crystals (Fig. 48f, Plate XIII) seem to differ from this form in that the long

sections are joined together by very small similar crystals.

The large fibres are the most interesting form. The number of these is much less than that of the other forms, but they are much larger than the single crystals. These particles are seen in greatest numbers and most fully developed in ammonium soap solutions.

They are always bent and very frequently twisted (Fig. 49c and d, Plate XIV). On one occasion the extraordinary form shown in Fig. 49e was observed; the particle has grown in the form of a knot. These photographs show beyond doubt that these fibres are ribbons rather than threads. They usually occur alone, but the cluster shown in Fig. 49f was observed in one solution.

It was found possible to draw a thread of solid on the end of a glass rod out of the clear but rather viscous solution of sodium stearolate. Such threads were up to 2 cm. long, and were seen under the microscope to consist of a very large number of fibres whose separate existence was only just visible at the teased-out ends.

The importance of these results lies in the assumption that the large particles of the solid soap are modelled on the form of the individual amicronic ones in solution: an assumption which is confirmed by the optical properties of the solutions mentioned on p. 86.

### *The Structure of Soap Solutions*

Soap solutions are classified by McBain<sup>1</sup> as follows:

1. A soap SOL is a transparent liquid whose viscosity may range from that of water to several thousand times that value.

<sup>1</sup> Darke, McBain, and Salmon, *Proc. Roy. Soc., A.*, **98**, 395 [1921].

2. A soap GEL is a transparent body having physical properties similar to those of a sol, except that it is elastic.
3. Soap CURD is a white more or less opaque mass of fibres holding sol or gel; the latter is also known as coagel.

Lamellar crystals may co-exist with any of the above forms.

In this book we are mainly concerned with sols; nevertheless, we cannot neglect these other forms of soap solution, which are so closely related.

One of the most remarkable points in a gel is the enormous amount of water bound in some way by the solute. One molecule of gelatin, for example, can hold in a rigid gel no less than 27,000 molecules of water. Soaps do not form gels so easily; in fact, the conditions for their formation are definitely limited.<sup>1</sup> 0.4 N sodium oleate gel could not be obtained at 0° C., nor could curd above 23°. 0.6 N gel and sol were not obtainable below 6° nor curd above 25°.

Soap gel is formed by cooling a sol or by warming coagel. When formed from sol there is no discontinuity of physical properties such as vapour pressure, electrical conductivity, refractive index, etc. On the other hand, conversion to curd is accompanied by a sharp change of all these properties. The only difference between sol and gel is that the latter is elastic. The nature of the soap particles in a coagel has been described.

Sol-gel transformation has been followed in a number of ways. The viscosity of a gelatin sol and the intensity of the Tyndall cone vary continuously and reversibly with temperature. When the sol is too dilute to gelatinise,

<sup>1</sup> Laing and McBain, *Journ. Chem. Soc.*, **117**, 1506 [1920]. Alexander, *Colloids*, p. 19.



similar changes of the Tyndall cone and the viscosity occur. Similarly, an optically inactive sol of benzopurpurin develops double refraction when electrolyte is added in quantity insufficient for coagulation; on heating, the double refraction disappears, but returns again on cooling.

In soap solutions continuity has been observed in a remarkable manner by the work of Hatschek<sup>1</sup> and Freundlich on viscosity. They find that certain sols are, in effect, elastic. They measured the viscosity of soap and other solutions by the Couette apparatus. This consists of two concentric cylinders, the space between them being filled with the substance under examination. The outer one is rotated at any desired speed, while the inner is suspended by a torsion wire carrying a mirror for measurement of the angular deflection due to the viscous drag. The angular deflection is theoretically equal to the product of the angular velocity and the viscosity.

They find, however, that at low angular velocity certain solutions, such as sodium stearate, have a viscosity which depends on the velocity of shear: the solutions, in fact, possess a degree of rigidity which, although insufficient to overcome gravity and endow them with a definite form, enables them to a certain extent to resist deformation by mechanical stress. The effect is particularly striking in the case of ammonium oleate solutions.

The matter is still further complicated by the behaviour of mixtures of soaps. It has been mentioned already that, occasionally, soap bubbles do not remain perfectly liquid; the black boundary does not remain sharp and the colour bands lose their mobility. This behaviour was attributed to the presence of quite small amounts of impurities, such as palmitic and stearic acids. The ammonium salts of these acids do not, however, show elasticity at all.

<sup>1</sup> *Kolloid Zeitschr.*, **13**, 88 [1913]; W. R. Hess, *loc. cit.*, **27**, 154 [1920].

Nevertheless, Freundlich and Kores<sup>1</sup> have recently shown that a mixture of soaps may possess rigidity out of all proportion to its constituents. A solution containing 0.44 per cent. sodium oleate and 0.1 per cent. sodium stearate is strongly elastic, whereas sodium oleate alone is not elastic and sodium stearate only very slightly so at this concentration.

This elasticity has also been observed by following microscopically the movements of a small nickel particle under the influence of an electro-magnet.<sup>2</sup> If the magnet acted for a sufficiently short time, the deflected particle returned to its original position on cutting off the force. From the movements of the particle under various conditions the elasticity of the solution could be determined. In this way the lack of elasticity of sodium oleate solutions was confirmed. Doubly refracting benzo-purpurin sol was found to be elastic. The elasticity of this and similar solutions is shown by the fact that the double refraction does not disappear immediately on stirring.

This continuity of properties from sol to gel shows that the soap is present in the latter as the disperse phase, and therefore disproves the early suggestion that the gel\* consisted of a sort of honeycomb structure of soap containing the water in the cells. Gel formation must be a result of the attractive forces between the micellæ and the solvent. The powerful nature and specific action of these forces may be illustrated by a single example. Aged sols of ferric oxide contain lamellar particles; these settle down at the bottom of the container in layers so regularly spaced that they appear a brilliant iridescent green. This is due to interference

<sup>1</sup> *Kolloid Zeitschr.*, **36**, 241 [1925].

<sup>2</sup> *Zeitschr. f. Phys. Chem.*, **104**, 233 [1923].

and, being a green of the second order, means that the layers are no less than  $250\ \mu\mu$  apart. An electric current passed through them normal to their plane causes them to close in until the colour appears red of the first order.

It is difficult to avoid the conclusion that the formation of gels and the preliminary stages just described are a result of the presence of thread-like particles. Such particles have been detected in solutions of substances so diverse as quinine, lithium urate, barium malonate, fibrin, and benzopurpurin. It is not suggested that such particles are necessary for gel formation; there is no evidence of their existence, for example, in gelatin gels; nor, indeed, is there sufficient evidence to be certain that gelatin and soap gels have the same structure.

Finally, it must be remembered that there is no reason for assuming that the colloid particles are modelled on the form of their constituent molecules. The substance which has been proved most convincingly to contain these threads is vanadium pentoxide.<sup>1</sup>

<sup>1</sup> See Freundlich, *New Conceptions in Colloidal Chemistry*, chap. vi.

## CHAPTER VI

### SOAP MOLECULES

LAPLACE's conception of surface tension requires the existence of a "radius of molecular attraction" larger than the objective size of the molecule. The earliest estimates of the dimensions of atoms and molecules were made on the assumption that they were spherical.

It is now known that the size of a molecule cannot be adequately expressed as a radius of a sphere; the corollary that there is no such thing as a definite radius of molecular attraction is not so fully realised.

According to modern theory, the objective atom is the space over which the electrical forces constituting it are acting. The incomplete equilibration of these forces as a result of spatial limitations is the origin of the residual forces responsible for inter-atomic and chemical attraction. Atoms, either packed into a crystal or a liquid or in their collisions in the gaseous state, approach one another to a certain distance and no closer; it is convenient to call the distance separating their centres (assuming them to be spherical) twice their radius, *i.e.* their diameter.

The attractive forces around the atom fall off very rapidly at small distances; according to Van der Waals the force is inversely proportional to the fourth power of the distance. We cannot define the radius of molecular attraction more specifically than as the distance over which the attractive forces remain large enough to manifest themselves.

Perhaps, logically, it would be more correct to call the "radius of molecular attraction" the "radius of the atom" (or molecule). In this case we should have the

diameter of the atom larger than the distance separating their centres; or in other words, the atoms (and molecules) are interpenetrating and the properties of liquids and solids more readily understandable than with the orthodox open-structure billiard-ball conceptions of matter.

In any case, we cannot expect these atomic dimensions to be independent of the conditions under which they are measured. Chromium and manganese provide an extreme example; the atomic radii of these two substances (from X-ray measurement) differ according to whether they are functioning as electro-positive or negative elements.

The majority of molecules, and especially those of the soaps, are very far from spherical. We have only reached our present state of knowledge of the reality of molecules by consideration of the implications of the form of individuals.

### *The Form of Long-chain Molecules*

Organic chemistry requires the existence of a characteristic form, in space, for every molecule. The long-chain compounds forming the soaps are an extreme and simple case of this, falling into a class by themselves. The naming of the normal substances "straight-chain," in contradistinction to their branched-chain isomers coupled with the conventional representation of their formulæ,

Normal valeric acid     $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ .

Iso                    "                    "     $\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \text{CH}_3 \end{array} \text{CHCOOH}$ .

Tertiary            "                    "     $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{C} \begin{array}{c} \text{CH}_3 \\ \text{COOH} \end{array}$ .

obscures that fact that they are really zigzag, as in Fig. 50, Plate XIV.

The big balls are the carbon atoms and the small hydrogens. The two medium-sized ones at the right-hand end are the oxygens of the carboxyl group.

The tetravalency of carbon has led to the idea of a symmetrical disposition of the valency bonds in space; that is, in the direction of the apices of an imaginary tetrahedron at whose centre the carbon atom lies. The plane angle between the valency bonds is therefore  $109^{\circ} 28'$ .<sup>1</sup>

Baeyer has pointed out the importance of this angle on the stability of ring systems. The angle between the bonds forming the ring of a member of the cyclomethane series depends on the number of carbon atoms in the ring. There will be least strain and, consequently, greatest stability where the polygonal angle is nearest to the tetrahedral angle. Table IX shows that cyclopentane, whose ring is, of course, a pentagon, is the member in which there is least strain.

TABLE IX.

Name.	Number of carbon atoms.	Polygonal angle.	" Strain " /bond.
"			
Cyclopropane .	3	$60^{\circ}$	$24^{\circ} 44'$
„ butane .	4	$90^{\circ}$	$9^{\circ} 44'$
„ pentane .	5	$108^{\circ}$	$0^{\circ} 44'$
„ hexane .	6	$120^{\circ}$	$5^{\circ} 16'$
„ heptane .	7	$128^{\circ} 34'$	$9^{\circ} 33'$
„ octane .	8	$135^{\circ}$	$12^{\circ} 46'$

<sup>1</sup> In the hydrocarbon chain each C atom is attached to two other C and two H atoms. The zigzag angle is not therefore that of a regular tetrahedron. Recent X-ray examination of a hydrocarbon crystal (Müller, *Proc. Roy. Soc., A.*, **120**, 437 [1928]) puts this angle at about  $84^{\circ}$ .

In accordance with this theory, cyclopentane is the most stable member of the series. For example, benzene when reduced by hydriodic acid at 300° C. forms methyl-cyclopentane and not cyclohexane as might have been expected. There is a very large amount of similar chemical evidence in favour of this theory. It may be recalled, also, that the lowest member of the naphthenic acid series is methyl-cyclopentane-carboxylic acid.

This conception of the tetrahedral angle, originally proposed on purely chemical grounds, has recently received a remarkable extension and verification by new methods of X-ray investigation.<sup>1</sup>

Long-chain substances, when melted or pressed on to a suitable support, act as diffraction gratings to X-rays. A number of orders of spectra are obtained from which the "spacing" of the grating can be calculated. Actually, several spacings are found, one of which is much larger than the others. This long spacing is found to vary with the nature of the substance under examination. In a homologous series it is a function of the number of carbon atoms in the chain, though odd and even members may form two separate classes. This is the case with the fatty acids, as is to be expected from the alternation of their other physical properties. A comparison of the spacings for a large number of substances shows that the results clearly fall into two classes, one being about twice the magnitude of the other. Table X gives the long spacings of a number of substances containing a chain of 18 carbon atoms.

<sup>1</sup> Müller, *Journ. Chem. Soc.*, **123**, 2043 [1923]; Shearer, *loc. cit.*, 3152; Müller and Shearer, *loc. cit.*, 3156; Saville and Shearer, *Journ. Chem. Soc.*, **127**, 591 [1925]; Müller and Saville, *loc. cit.*, 599; R. E. Gibbs, *Journ. Chem. Soc.*, **125**, 2622 [1924].

TABLE X.

	Å Units.
Octadecane . . . . .	{ 25.9
	{ 23.85
Stearonitrile . . . . .	25.0
Ethyl-pentadecyl ketone . . . . .	25.2
Hexyl-undecyl ketone . . . . .	25.2
Ethyl palmitate . . . . .	23.2
$\alpha$ Brom-stearic acid . . . . .	36.6
Stearic acid . . . . .	39.6
Oleic „ . . . . .	36.2
Elaidic „ . . . . .	48.3
iso-Oleic acid . . . . .	35.9
Stearolic „ . . . . .	40.5
$\alpha$ Hydroxy-stearic acid . . . . .	43.1
$\theta$ di-Hydroxy-stearic acid . . . . .	42.7
Stearamide . . . . .	37.3
Octadecyl alcohol . . . . .	42.1
Octadecylamine hydrochloride . . . . .	36.2
Methyl-hexadecyl ketone . . . . .	50.0

These results show that, in general, the presence of a chemically active end group doubles the spacing. The substances giving the doubled spacing are just those which are known to be associated in non-aqueous solvents. The conclusion that the pairs of molecules are held together by the active end groups is supported by measurements of the relative intensity of the different orders of spectra.<sup>1</sup> It is therefore suggested that the long spacing is the length of the single or double molecule, as the case may be, multiplied by an unknown factor.

A few of these substances have been obtained in the form of single crystals, and by X-ray examination of these Müller<sup>2</sup> has been able to elucidate the relation between the long spacing and the true length of the molecule.

<sup>1</sup> Shearer, *Proc. Roy. Soc., A.*, **108**, 655 [1925].

<sup>2</sup> *Proc. Roy. Soc., A.*, **114**, 542 [1927].



The fatty acids crystallise in flakes; the crystal cell contains four molecules arranged in equally spaced parallel sets, whose distance apart is considerably greater than the distance between successive carbon atoms in the chain. The basal plane of the crystal lies in the surface of the flake. The axis of the molecule chain lies at an angle  $\beta$  to the basal plane. Table XI gives the value of  $\beta$  for some fatty acids and for a hydrocarbon.

TABLE XI.

Substance.	$\beta$ .	$l$ .	$l$ (calculated).
Stearic acid . . .	63° 16'	48.84 Å.U.	46.1 Å.U.
Stearolic „ . . .	53° 4'	49.14	46.1
$\alpha$ Brom-stearic acid .	43° 15'	52.88	46.1
Behenolic acid . . .	53° 30'	59.1	56.3
Octadecane . . .	90°	25.6	22.8

The third column gives the length of the axis of the chain, that is, twice the length of the molecule; while the final set of figures is the length calculated for a zigzag chain of carbon atoms of diameter 1.54 Å.U. (their size in diamond). The area per molecule in the basal plane is  $20.5 \times 10^{-16}$  cm<sup>2</sup>.

Unfortunately, no satisfactory results have been obtained for oleic acid by this method. This acid is liquid at room temperature, and the only measurement made is a long spacing of 36.2 for the frozen substance. Fig. 51 shows the long spacings of the soap-forming acids, saturated and unsaturated. It is clear that although the triply unsaturated stearolic acid has a similar chain to stearic, no definite conclusions can be drawn concerning oleic and its congeners. It may be mentioned that iso-

oleic acid, in which the double bond is in the  $\alpha\beta$  position, gives the same spacing as stearic.

The actual figures obtained for the long spacing are dependent to some extent on the manner of mounting and preparing the specimen under examination.<sup>1</sup> A number of comparable results have been obtained. Shearer finds for sodium palmitate, 43.1 Å.U.; Piper and Grindley<sup>2</sup> give for sodium palmitate, myristate, and

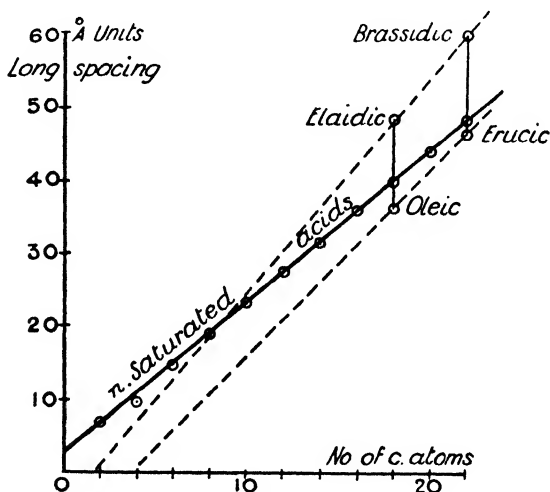


FIG. 51.—X-ray spacings of fatty acids.

laurate, 43.5, 38.5, and 33.5 respectively. De Broglie and Friedel find for "a smectic mass" of sodium oleate, 43.5.

Results of more direct bearing on the nature of soap films are provided by the study of thin oil films on water. The earliest experiments in this direction were made many years ago by Lord Rayleigh, Devaux, and others.<sup>3</sup>

<sup>1</sup> Piper, Malkin, and Austin, *Journ. Chem. Soc.*, **129**, 2310 [1926].

<sup>2</sup> *Proc. Phys. Soc.*, **35**, 269 [1923].

<sup>3</sup> *Proc. Roy. Soc.*, **47**, 364 [1890]. *Phil. Mag.*, (5), **31**, 362 [1897]. *Journ. de Phys.*, (4), **3**, 450 [1904]; (5), **2**, 699; 891 [1912]. *Nature*, **43**, 437 [1891]. *Annales de Physique*, (9), **1**, 19 [1914].

A known weight of oil dissolved in a volatile solvent is dropped on to a clean water surface; the area over which the oil spreads is measured by dusting talc on the water; this is driven back by the oil and the space covered by the film thus made apparent. In this way Devaux found a limiting thickness of  $1.10 \mu\mu$  for an olein layer.

Lord Rayleigh also observed that the thinnest possible oil films were unable to stop the well-known movements of camphor on the surface, but that compression of the oil film to twice this thickness immediately stops all motion. He also found that the thinnest layers affect the surface tension of the water but slightly; the double film, however, lowers it by a very large amount.<sup>1</sup>

The whole question of surface layers and of the spreading of liquids was in a very confused state until the work of Harkins and Langmuir.

Harkins and Feldman<sup>2</sup> get to the root of the matter by consideration of the factors involved in the spreading of a liquid over the surface of water. On the one hand we have the work of adhesion of the liquid to the water and, acting against this, the work of cohesion of the liquid itself. The decrease of free energy on spreading is numerically equal to the difference of these two quantities.

They find that almost all organic liquids spread on water, but that water spreads on very few. They show that the presence of certain end groups greatly increases the work of adhesion, but that such a group is not essential for spreading. They divide liquids into three classes:

---

<sup>1</sup> *Phil. Mag.*, (5), **30**, 386 [1890]; (5), **48**, 331 [1899].

<sup>2</sup> *Journ. Amer. Chem. Soc.*, **44**, 2665 [1922]. See also Bogue, *Colloidal Behaviour*. Section on "Surface Energy in Colloid Systems," by W. D. Harkins, **1**, 142-211.

1. Those that spread to a uniform polymolecular sheet.
2. Those that spread to a monomolecular layer, the excess remaining as a lenticular mass.
3. Volatile and soluble liquids.

Certain solids, such as myristic acid, may be included in the second class. Finally, they give a list of groupings according to their spreading activity. Active or polar groups which increase the adhesion of the liquid to water in order of decreasing efficiency:

OH, COOH, CONH, CHO, CN, CONH<sub>2</sub>.

And non-spreading groups:

Cl, Br, I, = S, CS, and phenyl.

For the formation of a monomolecular layer they postulate two requirements: a large coefficient of spreading and considerable molecular asymmetry. The reason for this second postulate is made clear by Langmuir's work.<sup>1</sup>

He regards the properties of a surface as the result of the residual valencies present in it; owing to the smallness of the radius of effective action of these forces, equilibrium is reached as soon as a monomolecular layer is formed. This monomolecular layer will have a definite structure. The polar group is attached to the surface of the water so that the long axis of the molecule stands up in the air. The most obvious result of this idea is that all the members of a homologous series will occupy the same area. This has been found to be the case by Langmuir's <sup>2</sup> own measurements and by the later more extensive work of N. K. Adam.<sup>3</sup>

<sup>1</sup> *Journ. Amer. Chem. Soc.*, **38**, 2221 [1916].

<sup>2</sup> *Ibid.*, **39**, 1848 [1917].

<sup>3</sup> *Proc. Roy. Soc., A.*, **99**, 336 [1921]; **101**, 452, 516 [1922]; **103**, 676 [1923]; **106**, 694 [1924]; **110**, 423 [1926]; **112**, 362 [1926]. A summary is also given in *Chem. Reviews*, **3**, 163 [1927].

The apparatus used by Langmuir and Adam consists of a shallow metal tray coated with paraffin wax and filled with water. A float on the clean water surface is attached to one arm of a suitable balance. The substance under examination is added on one side of the float and the area of the resulting film measured under various compressions,  $F$ . A curve of the form shown in Fig. 52 is obtained. The point  $A$  is supposed to show the formation of a close-packed oriented monomolecular layer. The

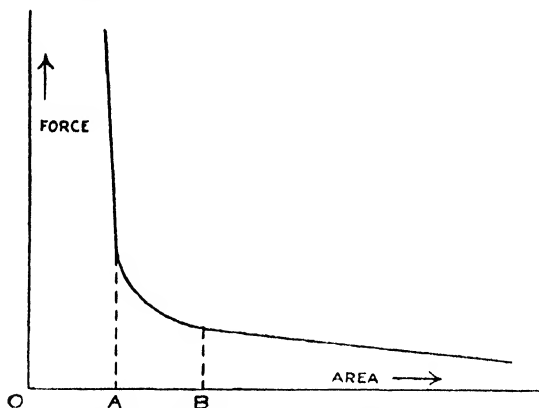


FIG. 52.—Compression curve of monomolecular layer on water.

compressibility is now very small, being about that of the substance in bulk. Certain substances form films which are treated as gases in two dimensions; that is, for small values of  $F$  they approximate to the "gas law"  $FA = RT$ . In the case of the fatty acids, the molecules cohere without external compression until the area per molecule is  $20.4 \text{ \AA.U. square}$ . Lateral molecular cohesion increases with length of chain.<sup>1</sup>

With this apparatus the length of the molecule can be obtained. If  $\omega$  is the weight of the acid spread over an

<sup>1</sup> Schofield and Rideal, *Proc. Roy. Soc., A.*, **109**, 76 [1925].

area  $A$ , and  $M$  its molecular weight, then the number of fatty acid molecules is  $\frac{N\omega}{M}$  ( $N$  being Avogadro's constant). The area per molecule is therefore:—

$$\frac{A.M}{N\omega} \quad . \quad . \quad . \quad . \quad (20)$$

If  $a$  is the area of the molecule so obtained (it will, of course, be the cross-sectional area) and  $\Delta$  the density of the substance (using the bulk value), then the length  $\lambda$  of the molecule will be:—

$$\frac{\omega}{A\Delta} \quad . \quad . \quad . \quad . \quad (21)$$

Table XII gives some of the results, the dimensions being given in Å.U.

TABLE XII.

Substance.	Adam.			Langmuir.	
	$\alpha$ chain.	$\alpha$ "heads."	$\lambda$ .	$\alpha$ .	$\lambda$ .
Myristic acid. .	21.0	25.1	21.1	..	..
Pentadecylic acid .	21.0	25.1	22.4	..	..
Palmitic        " .	..	..	..	21	24
Stearic         " .	21.0	25.1	26.2	22	25
Behenic        " .	21.0	25.1	31.4	..	..
Cerotic        " .	..	..	..	25	31
iso-Oleic      " .	21.0	28.7	26.2	..	..
Stearo-nitrile .	21.0	27.5	..	..	..

Adam distinguishes between the cross-sectional area of the polar groups and of the hydrocarbon chain, the latter being the smaller. The point  $B$  in Fig. 52 is supposed by him to represent close-packed polar groups. These, on

further compression, pack themselves away in such a manner that we finally get the uniform value 20.4 for the area of any close-packed long-chain compound.

If potassium permanganate is added to the water, unsaturated substances, such as oleic acid, no longer cohere to a liquid film but behave like a gaseous one. This is assumed to be due to the long axis of the molecule lying more or less in the plane of the water surface where, of course, they occupy a very much larger area and do not cohere.

The beautiful simplicity of these results is very striking, nevertheless it must not be forgotten that they require that the water should be slightly acid. In fact, it has been shown that the area over which a substance spreads is a function of the hydrogen-ion concentration of the water, being at a maximum at the iso-electric point.<sup>1</sup> Similar results have been obtained for  $\lambda$  on the surface of mercury. Oleic being 11.2, elaidic 12.2, while capric is 13.6, and stearic 22-24 Å.U.<sup>2</sup>

### *The Dimensions of Soap Molecules*

The dimensions of the sodium oleate molecule have been calculated from the amount of soap required to emulsify kerosene on the assumption that the soap is present as a monomolecular layer in a stable emulsion. If the size and number of the kerosene particles is known, the area covered by the soap molecules, and hence their length, is easily calculated. In this way the length of the sodium oleate molecule was found to be 48 Å.U., sodium stearate and palmitate were 27 and 30 respectively.<sup>3</sup>

<sup>1</sup> *Trans. Faraday Soc.*, **71**, 477 [1926].

<sup>2</sup> Shepperd and Keenan, *Nature*, **121**, 982 [1928].

<sup>3</sup> Griffin, *Journ. Amer. Chem. Soc.*, **45**, 1648 [1923].

A much more accurate and direct method of estimation of the dimensions has been used by de Noüy. His results of the time taken for the formation of a surface layer of minimum surface tension has already been mentioned (p. 10). He also found that the surface tension/concentration curve exhibited three pronounced minima corresponding to 1 part of soap in 750,000, 1,220,000, and 1,390,000 parts of water. He assumes that these concentrations give the amount of soap required to form monomolecular layers with the molecules in the three possible positions. The most concentrated solution, of course, corresponds to the monomolecular layer with the axis of the chain normal to the surface. From these results the dimensions of the molecule are  $12.3 \times 7.56 \times 6.64$  Å.U. From this result  $N$  can be calculated and the value obtained for it agrees with other estimates. De Noüy assumes that the surface layer consists of adsorbed sodium oleate. At the dilutions employed, however, hydrolysis is certainly complete. The dimensions are therefore those of the molecule of oleic acid.

Now although the calculated length is so small compared with X-ray results, nevertheless four times the volume calculated from these figures approaches very closely Müller's value for the unit crystal cell.



## CHAPTER VII

### THE COMPOSITION AND STRUCTURE OF THE SOAP FILM

WE have seen that soap solutions possess a specific surface layer differing in properties from the interior of the liquid. The idea that the stability of the soap film is due to this surface layer was first proposed by Marangoni. He argued that the centre part of a liquid film should fall freely under gravity. That it does not do so, he attributed to the formation of a "pellicle" at each surface by the action of carbon dioxide on the solution.

In place of Marangoni's obviously inadequate suggestion of the responsibility of carbon dioxide for the formation of the pellicle, Lord Rayleigh states<sup>1</sup> that "the capillary forces are themselves quite capable of overcoming weak chemical affinities and will act in the direction required."

He also states that the skin regulates its thickness, and hence the surface tension of the film, so as to compensate for the greater downward pull of gravity in the lower parts of it. Thinning then takes place subject to the ordinary laws of fluid viscosity; that is, at a rate proportional to the fourth power of the thickness of the film.

The sentence quoted says, in effect, that the capillary forces are capable of *initiating* chemical reactions. Since Lord Rayleigh wrote this, much experimental evidence of surface actions has given us fresh information of the process of adsorption. Surface-tension considerations can displace chemical equilibrium<sup>2</sup>; if the area of a mass

<sup>1</sup> *Proc. Roy. Soc.*, **47**, 281 [1890].

<sup>2</sup> It seems quite possible that capacity for reducing free surface energy is the determining cause of the preferential formation of one of two

of solution containing a number of components in hydrolytic equilibrium is increased there will be an increase of the amount of the component which has the lowest surface tension. Since, however, the maximum lowering of surface tension is effected by a surface layer two molecules thick, the amount of displacement of chemical equilibrium is exceedingly small even in the most extreme case, that of a soap film.

Moreover we do not require the assumption that there is a progressive alteration of the surface tension of a vertical soap film to compensate for the gradually increasing downward pull of the interior liquid. This downward pull is entirely taken up by the tensile strength of the liquid which, of course, results from the intrinsic pressure.

It is instructive to compare the soap film with Berthelot's experiments illustrating the tensile strength of liquids. He filled a tube almost completely with air-free water, leaving a small bubble of water vapour. The tube was sealed and then warmed until the water had expanded sufficiently to fill the tube. On cooling, the bubble of vapour did not re-form, showing that the liquid must have stretched. If the tube was not sufficiently strong it collapsed; in the soap film we have quite flexible walls with a rigid support at top and bottom.

### *The Surface of Soap Solutions*

Three terms have been used so far to describe the same thing: specific surface layer, pellicle, and skin. The

isomers, especially in Nature where reactions are largely surface ones. For example, oleic acid occurs in vegetable and animal fats in enormous quantities, but its geometrical isomer, elaidic, is quite unknown naturally. Similarly in the case of erucic and ricinoleic acids, the corresponding isomers are not found.

crude mechanical analogue of an elastic skin is most frequently used; saponin bubbles are cited to demonstrate its existence.

A bubble blown from saponin solution is, at first sight, similar to a soap bubble; very little thinning, however, goes on, and the regular sequence of colour bands characteristic of the soap film is never formed. But the greatest difference appears when the bubble is contracted by sucking the air out of it. The existence of surface skins becomes obvious from the extraordinary puckering which develops, while the liquid from the interior is squeezed out to form a drop at the bottom of the bubble. Fig. 53, Plate XV, shows two successive stages of the contraction of a saponin bubble. If left to itself such a puckered bubble quickly regains a nearly spherical form.

But this is not the behaviour of a soap bubble. All that this experiment shows is the fallacy of speaking or thinking of the surface layer of a soap solution as a "skin."

We have already seen that the specific surface layer of soap solution is formed by the process known as adsorption.

### *Adsorption*

The amount of solute adsorbed is usually calculated from surface-tension data by a simplified form of the Gibbs' equation, which has already been discussed on p. 80. For dilute solutions, Van t'Hoff's Law states that:

$$\frac{dP}{dc} = R.T.$$

We therefore get for the Gibbs' equation

$$a = \frac{C}{R.T} \cdot \frac{d\sigma}{dc} \quad . \quad . \quad . \quad (22)$$



FIG. 53A.

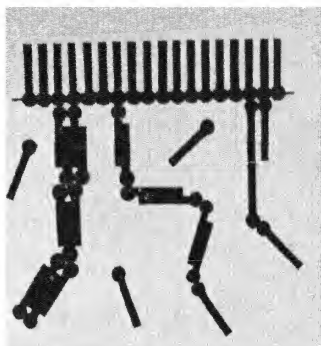


FIG. 55. Adsorption layer (McBain).



FIG. 53B.

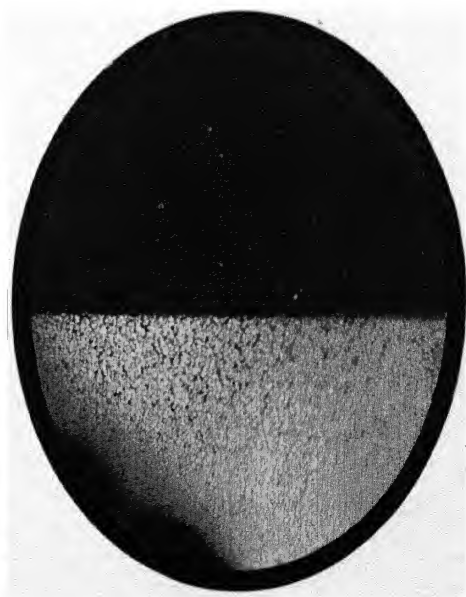


FIG. 56.—Critical fall —final stage.

FIGS. 53 A and B.—Contraction of saponin bubble.



Experimental determinations of the amount of adsorption have yielded results of the same order of magnitude as predicted, but it is only recently that a really accurate estimate has been made.

McBain and Davies<sup>1</sup> have measured the amount of

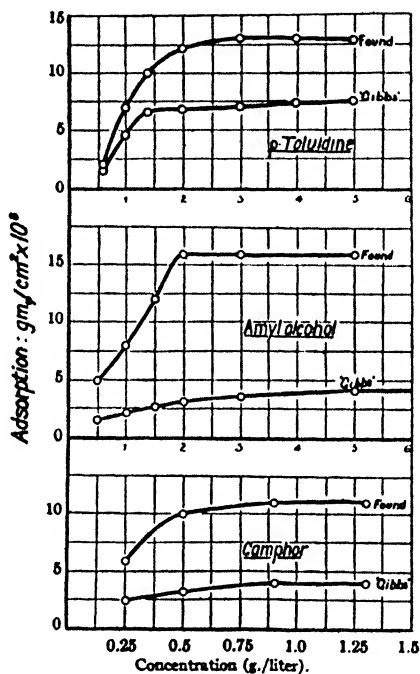


FIG. 54.—McBain's adsorption results.

adsorption at the surfaces of aqueous solutions of para-toluidine, amyl alcohol, and camphor. They find the amount adsorbed to be about twice that predicted by equation 22. Fig. 54 shows their results compared graphically with the amount calculated from the simple Gibbs' equation. It is also clear that the

<sup>1</sup> *Journ. Amer. Chem. Soc.*, **49**, 2230 [1927].

adsorption layer becomes saturated at quite low concentrations.

If this were a monomolecular layer, then the area occupied per molecule would be  $14 \times 10^{-16}$  sq. cm. for para-toluidine and  $9 \times 10^{-16}$  sq. cm. for amyl alcohol. The values found by Adam for the area occupied per molecule in the close-packed surface layers of the higher insoluble homologues are  $24 \times 10^{-16}$  and  $21 \times 10^{-16}$  sq. cm.

On this evidence the authors conclude that there is not only a monomolecular layer as suggested by Langmuir, but that, in addition, there is nearly as much again attached in some irregular manner after the style of iron filings clinging to a magnet (Fig. 55, Plate XV).

#### *Adsorption in Soap Solutions.*

We have seen that the surface-tension/concentration curves for the soaps fall steeply, bend round, and then rise very slightly. An application of the Gibbs' equation would suggest that positive adsorption only occurs in dilute solutions, and that above a concentration of about 0.5 per cent. soap a slight negative effect sets in. Nevertheless, the actual value of the surface tension is still very small, which, as we have seen, is due to the existence of the specific surface layer.

The cause of this anomaly is the inapplicability of the simplified Gibbs' equation to any solution containing more than two components. It also ignores all electrical effects. The adsorbed layer in soap solution contains excess of acid; the corresponding alkali is certainly exerting some influence.

McBain<sup>1</sup> has recently determined experimentally the amount of sodium oleate adsorbed. He determines the

<sup>1</sup> *Colloid Synopsis*, Toronto, 1928.

amount of acid and of alkali in the surface layer, and finds an excess of the former; the average composition of the material adsorbed from a neutral solution being  $1 \text{ Na}\overline{\text{O}}\text{I} : 0.7 \text{ H}\overline{\text{O}}\text{I}$ .

The calculated area occupied per oleic acid radicle is 11 sq. Å.U. If we assume that the fatty acid molecules are close packed, then the cross-sectional area is, as we have seen, about 21 sq. Å.U. The natural conclusion is that we have a double layer similar to those mentioned in the last section.

We cannot be certain, though, that the oleic acid radicles are occupying such a small area. However, the larger the area occupied per molecule the deeper a surface layer containing a given number must extend, so that we may certainly assume that the minimum depth corresponds to a layer of at least twice the depth of the monomolecular one.

The Gibbs' adsorption equation leads to another theoretical result. In a solution containing more than one solute, the one which depresses the surface tension most will be preferentially adsorbed. Saponin solutions are frequently cited as an example of this; an extremely small amount of soap is sufficient to prevent the appearance of the characteristic "skin." Saponin solutions are not, however, a fair example: the formation of the skin is not pure adsorption. The amount of saponin required to form the surface of minimum free energy is first formed; it is then transformed in some way so that it does not exert its full surface tension-lowering effect, and in consequence more adsorption takes place until most of the solute has found its way into the surface "skin." The difficulty of reepitisation of this skin proves that some transformation has taken place. The assumption that only one substance will be found in the adsorbed



layer is a consequence of the hoary old myth that the properties of a mixture are the mean of those of its constituents. The depression of surface tension is the result of the formation of a specific surface layer which possesses a definite structure. Measurements of the surface tension of mixtures of soaps in water show that two substances can form an adsorbed layer of smaller free surface energy than either of them alone.<sup>1</sup>

The bearing of this on the need for the use of perfectly pure solutions is clear.

The Gibbs' equation gives us some information about surface layers in general. An experimental relation between the lowering of surface tension caused by a solute and its concentration,  $c$ , has been found by Szyszkowski:

$$\frac{\sigma}{\sigma_0} = 1 - B \log \left( \frac{c}{C} + 1 \right) \quad . \quad . \quad (23)$$

where  $\sigma$  is the surface tension of the solution, and  $\sigma_0$  that of the pure solvent;  $B$  and  $C$  are constants.

From this equation we get

$$-\frac{d\sigma}{dc} = B\sigma_0 \frac{1}{C + c}.$$

This can be substituted in the Gibbs' equation; which becomes

$$a = \frac{B\sigma_0}{RT} \left( \frac{c}{c + C} \right) \quad . \quad . \quad (24)$$

Langmuir applies this to Traube's Rule, which states that the surface activity of solutions of a homologous series increases regularly as we ascend it; and he shows that the amount of work required to bring one molecule of solute from the surface into the solution increases

<sup>1</sup> Walker, *loc. cit.*, p. 16.

by a constant amount per methylene group in the chain. He assumes this to mean that the molecules are arranged with their long axis in the plane of the surface; that is to say, forming a "gaseous" surface layer.

On the other hand, he calculates the area per molecule from these two formulæ. In equation 23,  $C$  may be ignored for large values of  $c$ , and so we get for the amount of solute in the saturated surface layer

$$a_s = \frac{B\sigma_0}{RT} \quad . \quad . \quad . \quad (25)$$

This multiplied by  $N$  is the number of molecules per unit area, so that the area per molecule,  $A_\mu$ , is:—

$$A_\mu = \frac{RT}{N \cdot B \cdot \sigma_0} \quad . \quad . \quad . \quad (26)$$

The values so found for acetic and iso-butyric acids are  $30 \times 10^{-18}$  sq. cm.

The lowering of surface tension brought about by long-chain fatty substances is assumed by Langmuir to be due to orientation of the surface layer. This is a consequence of the kinetic theory. A substance forming a monomolecular layer consists, as we have seen, of a long hydrocarbon chain with a polar group at one end. This polar group attaches itself to the water surface; kinetic bombardment of the chain by water molecules will cause it to assume a position normal or nearly so to the surface.

Before going any further we must ask ourselves what is the connection between surface layers and soap films, or what is the difference between the layer adsorbed from a solution of a soap and an insoluble surface layer?

The process of adsorption is sometimes spoken of as a removal of solute from solution; the adsorbed layer is,

in fact, compared with the insoluble surface layer. The clearest proof of the incorrectness of this view is provided by the behaviour of cetyl sulphonic acid. As already mentioned,<sup>1</sup> this substance is soluble in water and the solution has all the properties of a soap solution.

McBain's analyses of the adsorbed layer suggest to him that we have to deal with a partial hydrolysis of adsorbed sodium oleate: addition of small excess of alkali completely prevents it.

However, McBain himself has shown how complex soap solutions are, and, in view of this work, the above assumption seems to be incomplete. I prefer to start by considering all the components already described in a soap solution and, from a knowledge of the properties of the surface layer and of soap films, decide which are essential.

We have then in a soap solution:

Water.

Molecularly dispersed soap.

Fatty ions.

Alkali ions.

Neutral micellæ.

Ionic micellæ.

As regards the properties of the surface layer, it is responsible in some way for the low surface tension of the solutions. It has an electrical conductivity large in comparison with that of the bulk of the solution; we have seen how this occurs in soap films. Taylor<sup>2</sup> has also observed that stirring up froth on a soap solution alters the conductivity which, however, returns to normal on collapse of the froth. The stability of films is very sensitive to excess of caustic soda and potash, but not to

<sup>1</sup> Page 19.

<sup>2</sup> W. W. Taylor, *Chemistry of Colloids*, p. 239 [1921].

ammonia; the smallest excess of the two former destroys the lasting-power of films completely. Finally, it may be mentioned that soap solution is never satisfactory for making films when freshly prepared; there is some ageing effect which requires a day or so.

### *Soap Films and Surface Layers*

Before coming to any final decision we must consider soap films, both black and coloured, and also the thinning processes. The conception of a soap film as a sheet of solution enclosed between two surface layers leads to the idea that the black is simply these two surfaces adhering as a result of the removal of the interior liquid by drainage. This is supported by a mass of evidence, but does not include all the phenomena which have been described earlier in this work. Let us restate briefly the thinning of a film.

The formation of a film requires the instantaneous formation of two surface layers, with consequent re-equilibration of the internal solution. Thinning of the film then proceeds as a result of the suction of the internal liquid into the Gibbs' ring or rings. When the film reaches a thickness of about  $300\ \mu\mu$  its electrical conductivity rises in a manner which suggests a progressive concentration of solute in the thinner film. When the film has reached a lower limit of about  $100\ \mu\mu$  a sudden decrease of thickness to about  $12\ \mu\mu$  occurs; this step-down may, however, occur much earlier in the history of the film. Solutions containing no glycerine also form a thinner black stage  $6\ \mu\mu$  thick.

We have also seen that there is another and quite different manner of thinning. This has been called the "critical fall," owing to its manner of appearance; definite evidence of the necessity of some stimulation,

usually by light, has been given. The two methods of thinning are entirely different; the slower the critical fall, the larger the black particles; extra rapid normal falls occasionally occur, but exhibit no signs of critical development. We can unhesitatingly reject the idea that the normal fall is a critical one on a microscopic scale.

When a film is examined microscopically, the development is almost always of the critical type; no doubt this is due to the necessity of concentrating light on the part of the film in the field of view.<sup>1</sup> Occasionally a normal fall does take place under the microscope. We can be certain then that the critical fall is the macroscopic analogue of the type of blackening described by Perrin and Wells and seen generally under the microscope.

The conclusion which I have reached is that the critical fall consists of a gradual breakdown of one of the surface layers; coalescence of the liquid film on the remaining surface layer follows as a result of surface tension. Black appears at a number of points and spreads all over the film. This theory may seem rather fantastic at first sight. For this, conventional ideas of surface tension are largely responsible. We are apt to confuse the phrase "breakdown of the surface layer" with the mechanical analogue of a stretched elastic membrane bursting with a loud report. By "breakdown" is meant substitution of a new set of surface conditions

<sup>1</sup> The thinning of a film of viscous solution, such as 5 per cent. ammonium oleate in 50 per cent. glycerine, illustrates the disturbing effect of the concentration of light required by the reflection microscope. Thinning takes place by aggregation of the internal liquid into spherulites; these shoot about the film, growing and coalescing until they have reached such a size that they sink to the bottom. They are easily visible, as their edges are defined by Newton's rings of high order; by a curious optical illusion, they appear to be ringed all over after the manner of Liesegang's rings.

which may well take place gradually and start at a number of points. Fig. 56, Plate XV, shows a late stage, on twice the scale of the other photographs, of a critical fall which supports this view. Any theory of the structure, stability, and behaviour of the soap film will be unusual because the soap film is an unusual thing. The critical fall is an astonishing display of molecular behaviour or, perhaps I should say, misbehaviour.

This conception of the critical fall requires that the final stage of thinning should be the first order of black, while films made from similar solutions, provided they contain glycerine, will generally only reach the second order twice as thick. Photometric measures suggest that this is the case.<sup>1</sup> In addition, the rate of formation of the five blacks increases as their thickness decreases, that of the second order being especially rapid; this shows that they are not enclosed between two surface layers and subject to the laws of fluid viscosity.

We can also understand why the black film formed by critical development never has a stability comparable with that formed by the normal process; critical blacks rarely last for more than an hour or so; frequently they break as soon as formed. The occurrence of a critical fall or its inhibition by a small amount of impurity depends, no doubt, on the viscous and elastic properties of the solution used.

### *Properties of the Black Film*

We must first ask whether the black film formed by normal thinning contains anything besides the two surface layers. Without any special definition of the surface layer we can answer this question at once, as a

<sup>1</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **24** (1), 221 [1923]; *Collected Papers*, **2**, 1352.

result of Reinold and Rücker's observation that addition of electrolyte to soap solution prevents the abnormal rise of conductivity which otherwise occurs in very thin films. Electrolytes, such as potassium nitrate which they used, are only negatively adsorbed; the fact that they are present in the thinnest films proves that these contain some interior liquid. The observation of Rickenbacher and Hagenbach that movement of the film prevents the abnormal rise of conductivity also requires the presence of interior liquid. Perrin also observed fluorescence in black films prepared from solution containing fluorescent blue.

Once a film has thinned to the black stage it is not at all easy to thicken it again. If, for example, a partly black bubble is contracted by sucking the air out of it, the black surface remains almost constant until its area is a large proportion of the total.<sup>1</sup> Any movement of liquid up into the interior of the black is, of course, subject to the laws of fluid viscosity, and the actual rate is therefore proportional to the fourth power of the thickness of the film which, in the case of the black, is an exceedingly small quantity. The thickness of the black is, however, curiously sensitive to temperature changes. Johonnott observed that the thickness of a black film increased very largely on cooling it. Some observations of Sir James Dewar also point to the reversibility of the thinning process. Fig. 57,<sup>2</sup> Plate XVI, shows the appearance of a black film left in the cube overnight in an atmosphere saturated with water vapour. Liquid from the small

<sup>1</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **22** (1), 202 [1917]; *Collected Papers*, **2**, 1197. The table given in this reference contains a misprint: for 302.5 in the second column, last line but one, read 320.5.

<sup>2</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **24** (1), 211 [1923]; *Collected Papers*, **2**, 1345.

PLATE XVI.

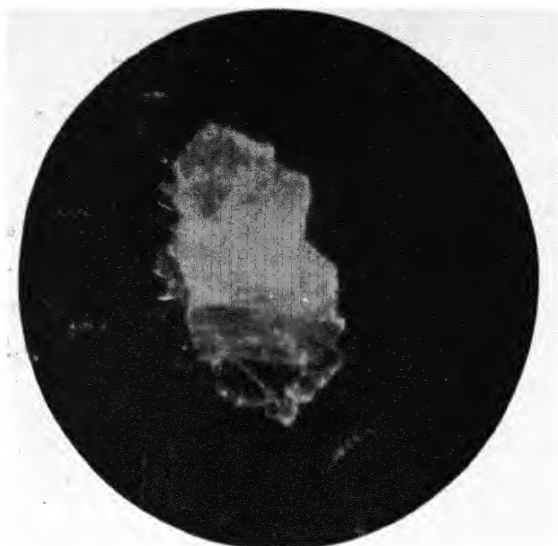


FIG. 60. Acid soap separated in crystalline plates.

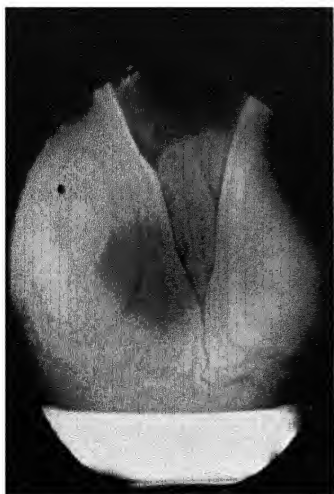


FIG. 57. Thickening of black film.



FIG. 58. Thickening of black film.





patch of silvery white at the bottom has clearly a connection with the thickening of the black to the grey stages shown (with the contrasts much exaggerated). Fig. 58,<sup>1</sup> Plate XVI, shows a rather different type of convective movement. This is also a photograph of a film which had stood overnight in the cube, the solution in this case being a viscous one. The permanence of the tracks, together with their form, suggests the presence of colloid threads.

Investigators of this subject have made great use of the idea of an elastic skin. Even Plateau attributed the stability of the soap film to its surface viscosity, while a more modern worker describes the surface layer as "a tough jelly-like skin."<sup>2</sup> The black film is not viscous, it is not tough, nor does it remotely resemble a jelly. The resiliency of a mass of foam is the result of its structure; it consists of a number of plane films connected by the ideal joints provided by the Gibbs' rings. Fracture of any one film only results in a small movement of re-equilibration of the neighbouring films.

The only direct evidence of the mobility and tensile strength of the black film is provided by some simple experiments made by Sir James Dewar. A film was formed on a 4-inch ring half-way down a deep glass cylinder. When it had drained to blackness, it was lifted into a horizontal position by means of a thread attached to the bottom of the ring. Various substances were then dropped on to it. Occasionally a lead shot passed through without damaging the film, but more usually the shock broke it. Similar results were obtained with soap solution and water drops. Mercury drops, if perfectly clean, passed through with less disturbance; on one occasion half

<sup>1</sup> Sir J. Dewar, *Proc. Roy. Inst.*, **24** (1), 223 [1923]; *Collected Papers*, **2**, 1354.

<sup>2</sup> Freundlich, *Colloid and Capillary Chemistry*, English trans., p. 796.

a dozen drops 1.5 mm. diameter passed without damage through a black film which had stood overnight. The slightest trace of fatty impurity on the drops always leads to rupture, even with thicker films. Almost anything can be dropped through a coloured film, especially if thick. Large lumps of caustic soda, a thin stream of water, liquid-air drops, and sulphuric acid all passed through apparently without effect. Anything moistened with oleic acid always broke the film. Whether the black film actually stretches or, as is more likely, the movement is taken up by the Gibbs' ring, these experiments show that we are not dealing with anything of the nature of a tough jelly-like skin.

### *Theories of the Constitution of the Black Film*

Apart from guesses, three theories have been proposed for the constitution of the black film. The first two are the outcome of the work of Perrin and P. V. Wells on stratified films. These two workers both take their rather special films as typical representatives of the normal form; they regard their stratifications as an extension of Johonnott's five blacks. The descriptions given here of stratification and of the properties of Johonnott's five blacks show that these are totally different phenomena. However, the clearest proof of the difference of normally thinned and stratified films is shown by the difference of the figures for the limiting thickness of the black. For normally thinned films we have about  $6\ \mu\mu$ , while Perrin gives 5.2 and Wells 4.2. Incidentally, the difference of the results of these two workers requires explanation. Their views on the nature of the surface layer are, of course, equally applicable to ordinary and stratified films. Both these workers assume that the adsorbed layer, and hence the black film, consists of oleic acid on evidence open to

criticism. Starting from the well-known fact that the surface layer of soap solution has an acid reaction, Perrin devised an experiment to measure the amount of acid present there. Air is bubbled through some soap solution in the bottom of a vessel standing in a photographic dish; the vessel is thereby filled with a mass of foam which then overflows into the dish. The air current is continued until the residual solution has become so poor in soap that durable foam is no longer formed. The liquid carried over as foam is then analysed. It contains, of course, water, soap, and oleic acid. Perrin makes the tacit assumption that the excess oleic acid is the adsorbed layer, while the neutral soap is carried over mechanically with the water in the interior of the film.

In this way, from a knowledge of the number and area of the bubbles and the weight of solute carried over, he arrives at a thickness for the surface layer of  $1.9 \mu\mu$ ,<sup>1</sup> for which he claims an accuracy of not less than 10 per cent.

From a comparison of this figure with the thickness of the black, he concludes that the latter consists of a bi-molecular layer of oleic acid held together by a sheet of water.

Such a structure has been obtained experimentally by Sir W. Hardy;<sup>2</sup> he finds that a film can be made by dipping a wire ring a few centimetres in diameter into water whose surface is covered by a monomolecular layer of oleic acid. These films are only stable when the film of fatty acid is about one molecule thick. Their properties, however, show that they differ essentially from true soap films. These films do not possess the ready extensibility

<sup>1</sup> This thickness means  $0.6 \times 10^{-9}$  equivalents per  $\text{cm}^2$ . McBain finds 1.5 equivalents, of which two-fifths are hydrolysed, thus giving exactly the same amount of excess oleic acid as Perrin.

<sup>2</sup> *Journ. Chem. Soc.*, 127, 1224 [1925].

of the soap film since there is no reserve of fatty material, the internal liquid being water. A more fundamental difference is indicated by Sir W. Hardy's statement that thinning is seen to be restricted to the interfacial liquid; this is certainly not the case in soap films.

Now, P. V. Wells obtains a final value of  $4.2 \mu\mu$  for the thickness of the black. He compares this with Langmuir's figure for the length of the oleic acid molecule,  $2.3 \mu\mu$ . He also points out the similarity of the thickness of the black formed from solutions containing widely different amounts of water, one being described as almost anhydrous. On this evidence he concludes that the black is an anhydrous bi-molecular layer of oleic acid.

However, this value for the length of the molecule is very doubtful. His so-called nearly anhydrous soap solution shows all the properties characteristic of aqueous soap solutions, and in addition glycerine is just the one substance capable of replacing water with least effect. In any case, consideration of stratification as crystallisation is quite sufficient to explain this similarity.

We have seen the almost overwhelming evidence for the presence of water; the formation of the structure suggested by this worker is not feasible at all. Sir W. Hardy has shown that the associated pairs of fatty acid molecules divide as soon as they can find company more congenial. The carboxyl group prefers even the inhospitable surface of bismuth to its own fellows. An ejection of water, such as the theory of P. V. Wells requires, is difficult to reconcile with this evidence. It is also difficult to see how such a structure could possess a surface tension equal to that of soap solution. Both these theories entirely fail to explain how a stratified film can become solid in absence of alkali; nor do they explain the high electrical conductivity of thin films.

The third one, due to Miss Laing, starts from this point.<sup>1</sup> She analysed a mass of froth and compared the results with those of the original solution. The analysis was complete in that acid and alkali were measured. From these results she was able to find the relative proportions of acid and alkali concentrated in the foam by adsorption. In neutral and acid solution she found that the composition of the solute in the foam was 1 Na $\overline{\text{O}}\text{I}$ ; 0.61 H $\overline{\text{O}}\text{I}$ . In alkaline solution equivalent proportions of acid and alkali were found. She concludes from these experiments that the black film consists of two surface layers of acid soap cohering as a result of thinning. She points out that the acid soap is probably hydrated, but that this has little effect on the dimensions of the molecule according to X-ray measurements. This theory is satisfactory enough for black films obtained from stratified films; it does not include, however, the results of all the other workers mentioned in Chapter III. This theory does not explain, either, how a film, even of small stability, can be formed from an alkaline solution.

From a survey of the facts Freundlich<sup>2</sup> arrives at a similar conclusion. He accepts Rickenbacher's suggestion that the surface layer, and therefore the black film, have a gel structure consequent on the presence of long threads of colloid soap. The high mobility of the black has been described, and this is a very good reason for assuming the absence of any neutral colloid in the black.<sup>3</sup>

<sup>1</sup> *Proc. Roy. Soc., A*, **109**, 28 [1925].

<sup>2</sup> *Colloid and Capillary Chemistry*, English trans., pp. 796 and 842.

<sup>3</sup> The absence of colloid threads in the black is further illustrated by the microscopic examination of critical blackening. The appearance of black spots at a number of points in a thin film and their subsequent spreading results in the sweeping up of the superfluous liquid into a sort of honeycomb structure. Its appearance and stability suggest that it contains the colloid threads. (See P. V. Wells, *loc. cit.*, p. 23.)

The formation of a film by lifting it out of a soap solution on a ring is probably sufficient to orient all the threads of colloid in the plane of the film; drainage will keep them in position until sucked into the Gibbs' ring. Their presence in the film oriented in this way is, no doubt, part of the cause of the greater strength of thicker films as compared with the black. Gel formation, which appears to be dependent (in the case of the soaps at any rate) on the presence of these long fibres, does actually take place in the Gibbs' ring. Films made from dilute aqueous solutions of sodium oleate often leave the Gibbs' ring behind as a ring of gel when they break. Gelatinisation of partially blackened bubbles has already been described: the black boundary becomes zigzag and the colour bands vertically streaked: only the coloured part is rigid.

### *The Nature of the Soap Film*

As we have seen, the problem of the soap film is really a triple one: the nature of the black, of the coloured, and the relation between them. Now we have seen that the black probably consists of two surface layers, not separated but rather, held together by liquid. For this reason the arrangement of the solute adsorbed in the surface layer is important. The incorrectness of regarding a monomolecular layer of fatty acid on water as having a separate existence without any reference to the water has been mentioned. Orientation of fatty acid molecules equally implies orientation of water molecules. It may be observed that oleic acid, which forms a monomolecular layer on water, has a definite angle of contact with ice.<sup>1</sup>

Similarly, the specific surface layer, whether we call it a skin or adsorbed solute, must not be thought of as

<sup>1</sup> Pockels, *Physik. Zeitschr.*, **15**, 39 [1914].

having a separate existence. It is not the ideal static affair which we considered in the first chapter according to Laplace's ideas, but a dynamic one.

Sir W. Hardy has shown that films of some stability can be prepared from water covered by a monomolecular film of oleic acid; excess of fatty acid prevents this. This experiment may be taken to mean that film formation results from the presence of a monomolecular surface layer. The greater stability of the soap film is a result of the reserve of fatty substance *just beneath* the surface layer *in solution*.

McBain's estimates of the amount of adsorption show that the amount of this reserve is about equal to the amount in the surface layer. He suggests that the remainder is aggregated into chains attached to the surface layer at a number of points, the whole being in a state of flux as a result of the kinetic movements of the molecules.

A clue to the effective depth of the adsorption layer is provided by Johonnott's five blacks. Why five? The number required to bridge over the gap between the black and the silvery white is about fifteen.

First-order black . . . . .	6 $\mu\mu$
Second-order „ . . . . .	12 „
Fifth „ „ . . . . .	30 „
Silvery white . . . . .	c. 100 „

This suggests that the effective depth of the adsorption layer is about 15  $\mu\mu$ . The thickness of the fifth order of black, 30  $\mu\mu$ , reminds us that this is the approximate minimum thickness reached by aqueous solutions of soap containing no added electrolyte or glycerine. The greater amount of colloid in these films, and hence the greater degree of structure, explains the permanence of this thicker stage. Moreover, it is quite certain that much of



the solution used by those workers who have found these large thicknesses of black is impure. Reinold and Rücker, for example, complain of the stringiness of their solution, which was nominally sodium oleate. This is a sure sign of the presence of saturated impurities, stearic and palmitic. We have already seen the way in which rigidity is developed by addition of these saturated soaps to oleate. Most of the workers who have measured the thickness of the black regard the terms soap and sodium oleate as synonymous.

A rigid static conception of the surface layer would

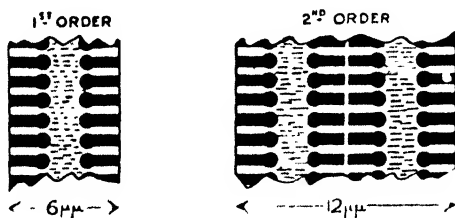


FIG. 59.--Sectional view of black film, diagrammatic.

give a picture of the black as in Fig. 59. The lack of any reserve of fatty material in the interior is no doubt the cause of the small stability of the first order of black as compared with the second. The higher orders certainly consist of a pair of monomolecular surface layers enclosing an equilibrated mixture of water, fatty ions, sodium ions, and neutral soap; there is little evidence to suggest how far these components are aggregated into colloidal micellæ. We saw earlier, however, that the higher members of the acetic series only form soap solutions near to the boiling-point: this suggests the need for solute not aggregated into colloidal particles. Glycerine which, as we have also seen, improves the film-forming capacity of

a soap solution also reduces the amount of colloiddally disperse soap.

The very much smaller value found for the thickness of stratified black films by Perrin and P. V. Wells is no doubt due to a lesser degree of hydration, if indeed there is any water present at all. A recent discovery throws some light on these stratified films.<sup>1</sup> Acid potassium oleate has been isolated in crystalline form. This is the first occasion on which an acid soap has been prepared, although the conception of these loose compounds dates back to the earliest work on the chemistry of the soaps. 139 grm. of oleic acid and 145 grm. of potassium oleate are dissolved in boiling alcohol and the solution made up to a litre. On cooling to 0° C., the acid soap separates in crystalline plates (Fig. 60, Plate XVI).

What exactly is the connection between this compound and the stratifications remains to be seen. It may be remarked that these stratifying solutions are very sensitive to excess of oleic acid, and on standing deposit oily anisotropic drops in a manner quite foreign to normal soap solutions.

This view of the black (Fig. 59) leads to a similar constitution for the coloured film, except that the latter contains an amount of water which gradually increases until, by the time the thickness has reached about 350  $\mu\mu$ , the concentration of solute in the interior is that of the bulk of the solution from which the film was prepared.

We still have to explain the sudden increase of thickness at the black boundary. In a well-drained film, the silvery-white stage which is in contact with the black is about 100  $\mu\mu$  thick; that is to say, there is a minimum increase of some 90  $\mu\mu$ . In thick films this increase may be several hundred.

<sup>1</sup> McBain and Stewart, *Journ. Chem. Soc.*, **131**, 1393 [1927].

The only attempt at explanation is that of Reinold and Rücker.<sup>1</sup> They point out that a soap film might be expected to behave in this manner if there were a difference of the surface tension of the part of the film next to the black, while the black itself had the normal value of the remainder of the film. This extremely artificial suggestion is not supported by their own experimental work, which points to constancy of surface tension right down to the thinnest stages. In any case, this theory would require the part of the film with variable surface tension to vary with the actual part in contact with the black.

An observation has already been described which throws light on this curious point. In the microscopic examination of a film the extent to which the Gibbs' ring extends into the film frequently shows itself as a circle of light; this is evidently a sudden increase of thickness similar, though on a larger scale, to that which occurs at the black boundary.

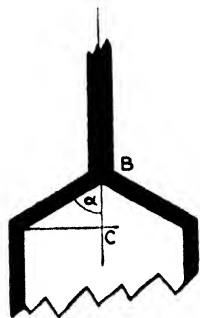


FIG. 61.-- Black boundary, diagrammatic.

We have seen that there are good reasons for believing that the blackening of a film under the microscope results from the breakdown of one of the surface layers. In other words, at the limit of the Gibbs' ring we have the familiar case of three films meeting, of course, at  $120^\circ$ . Suppose now we treat the black, whatever its thickness, as a single film; we then have a similar state of affairs at the black

boundary. Fig. 61 shows a diagrammatic view; it is clear that the angle  $\alpha$  will be  $60^\circ$ .  $BC$ , the distance in the plane of the film over which the gradient of increasing

<sup>1</sup> *Phil. Trans.*, **177**, 679 [1886].

thickness extends, is equal to the product of half the increase of thickness and the cotangent of  $\alpha$ , that is, 0.577. For a silvery-white film in contact with the black,  $BC$  will be 28  $\mu\mu$ ; the maximum value for  $BC$  with a film too thick to show colour in contact with the black will only be about half a micron.

This correlation of the sharpness of the black boundary with the conditions for equilibrium of intersecting films does not throw much light on the mechanism of the arrangement. Consideration of a mass of foam makes it clear that any arrangement with more than three films meeting along a line will be unstable, in that any small disturbance will cause elision of one of the foam cells until we have the familiar three left. Consideration of what further simplification would mean shows its impossibility. It is obviously impossible for two films to meet.

We have seen that soap is not just soap, but that the term covers a surprisingly wide range of properties. Soap films are correspondingly versatile. Much of the confusion which I have tried to unravel is the result of a fixed idea of a Protean uniformity of soap films which renders them susceptible of a simple all-embracing explanation. No one, chemist or not, would expect a black film prepared from a solution of sodium laurate to be the same as one from sodium stearate, yet the labelling of the filthiest samples of soap "sodium oleate" seems to inhibit the realisation of this difference. Many workers, with the notable exception of Sir James Dewar, have taken insufficient care for the purity of their soap; this makes comparison of their results uncertain.

The chief lesson provided by the study of the soap film is the necessity of considering individual molecules. The atomic theory is too often no more than a mental reservation that matter is ultimately discrete rather than

a starting-point for the understanding of the properties of matter in bulk.

We have to consider not molecules as individually free units, but the mutual effects of the individuality of any one molecule on those surrounding it, like or unlike; in fact, the limitations of its freedom.

The individuality of soap molecules is so peculiar that they may be described as eccentric. By various workers they have been credited with heads and tails, although they prefer to stand upon the former. Indeed, they appear to try to emulate the ostrich and bury their heads in the most unlikely surfaces while the rest of their body, which only consists of a tail, sticks up in the air. This type of anthropomorphic familiarity, however picturesque, should only be indulged in with caution. Adsorption is sometimes spoken of as a movement of molecules to the surface layer to reduce the surface tension. The implied endopsychic endowment of the molecules is quite unjustifiable.<sup>1</sup> Molecules arrive at the surface as a result of their own kinetic wanderings; when oriented into a specific surface layer, the free surface energy is at a minimum. Subsequent passage of a molecule into the interior would entail an increase of free surface energy, and therefore does not take place except by the normal method of reduction of surface.

It was pointed out early in this book that surface tension is antagonistic to the stability of the soap film. Clearly surface tension is not following its usual contractile course because the free surface energy of a soap solution is preferentially reduced by adsorption. This is easily understood when we remember what a small amount of solute is required to form the surface of minimum free energy. Stability of the film requires that

<sup>1</sup> Cf. p. 108.

the effective strength of the surface layer should be greater than the value to which the surface tension of water is reduced by the soap. In the homologous fatty acid series we have seen that this first occurs at lauric, which contains a chain of twelve carbon atoms. There is every reason to suppose that lower members are also oriented; we must assume, therefore, that their length of chain is insufficient to lower the surface tension below the effective strength of the surface layer.

Sufficient has been said to show the importance of orientation in the soap film, though one special point remains. The abnormally high electrical conductivity of thin films is reduced to normal by mechanical agitation, and so must follow from some definite arrangement of the interior liquid; the nature of this structure remains obscure, indeed the point has never even been considered. Other problems awaiting investigation are the nature of the process of stratification and the trigger action of light in starting a critical fall.

The peculiarities of ammonium oleate solutions have been referred to several times; the constitution of these, and also of the solutions which give stratifying films, require elucidation. Finally, except by analogy, nothing is known of the capacity of the fatty acids other than oleic to form black films, except that Perrin has prepared them from the pseudo-soap solutions furnished by the resin acids.

## APPENDIX I

### OLEIC ACID

It has been pointed out repeatedly that soap solution must be prepared from chemically pure oleic acid, otherwise endless troubles and complications occur. The commercial product is occasionally quite pure, but more usually very bad.

The reason for this lies in the difficulty of purifying this substance; owing to its low melting-point it cannot be purified by crystallisation, nor can it be distilled either under atmospheric pressure or *in vacuo* owing to its high molecular weight and, therefore, boiling-point. This difficulty is the cause of the paucity of accurate information about the acid and the origin of numerous properties incorrectly ascribed to it. The following details of the purification of crude oleic acid may be useful, and also show the danger of regarding any sample of "pure oleic acid," whatever its credentials, as free from suspicion of adulteration.

The impurities present in any sample of oleic acid fall into three classes:

1. Unsaponifiable; that is, substances not converted into soap by alkali.
2. Saturated acids of the acetic series; mainly stearic and palmitic.
3. Acids less saturated than oleic; that is, those containing more than one double bond.

The methods of purification proposed all make use of the fact that the solubility of the salts of the fatty acids are proportional to the unsaturation of the acids. It may be mentioned that elaidic, the geometrical isomer of oleic, behaves in this respect like the saturated acids; it is fortunately rare in any case.

The usual practice is to extract the unsaponifiable from the aqueous solution of the potassium soap by ether; or better by petroleum ether from the 50 per cent. alcoholic solution.

The next stage consists of conversion into the lead salt by addition of aqueous solution of lead acetate. The insoluble precipitate is then separated and the lead salts of the unsaturated acids dissolved in ether. This ethereal extract will contain class 2 and 3. To separate these, advantage is taken of the greater solubility of class 3 in benzene. The mixed barium salts are

dissolved in benzene containing a trace of water; on cooling, the oleate separates out in crystalline form. The purity of this final product is not satisfactory, nor is this process workable except with very small quantities. The following system was therefore developed.

The separate extraction of unsaponifiable was omitted, as these substances remain behind in the mother-liquors of the barium salt crystallisation. The fractional solution of the lead salts of the unsaturated acids was rendered more efficient and applicable to large quantities by the following process.

Crude oleic acid is heated to  $100^{\circ}\text{C}$ . and then one-tenth of its weight of litharge added; solution is complete in a few minutes. While still warm six times its volume of ether is added and the clear solution left to stand overnight.

The molecular weights of all the acids likely to be present are in the neighbourhood of 280, and as they are all monobasic it can be seen that the amount of lead oxide added is only sufficient to convert about a quarter of the fatty acid into lead salt. The result is that the lead salts of the saturated acids separate out in a crystalline form, and can be separated from the ethereal solution of oleic acid and a little lead oleate by means of the filter-pump, provided a coarse paper is used. In the orthodox lead salt-ether process we have to separate a strong solution of lead oleate from a sludge of lead salts of saturated acids; the attempt to do this on the filter-pump results in a mess which has to be seen to be believed.

The efficiency of this modified method is greater not only as regards yield and ease of working, but, as the lead salts of the saturated acids are slightly soluble in the strong ethereal solution of lead oleate and not so in the ethereal solution of oleic acid, in the more complete removal of saturated acids. For this reason the amount of ether used should not be reduced below the limit given.

Another improvement of the lead salt-ether process has been described.<sup>1</sup> The mixed lead salts are boiled with some lead acetate in toluene solution; this solution is cooled to  $-10^{\circ}\text{C}$ ., which makes the insoluble lead salts sufficiently crystalline for separation by the filter-pump.

The barium salt crystallisation is improved by boiling oleic acid with the requisite amount of barium hydroxide in a mixture of equal volumes of toluene and amyl alcohol containing a trace

<sup>1</sup> Lapworth and others, *Biochemical Journal*, **19**, 7 [1925].



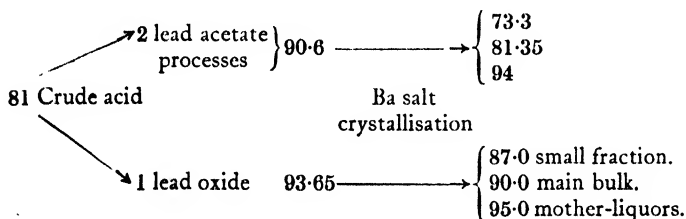
of water. The authors of this paper complicate the working of the chemical method of purification by interposing odd vacuum distillations which would be probably better omitted.

The lead salt-ether method, even improved as described, leaves very small traces of saturated acid, especially palmitic, which are naturally concentrated in the crystallisation of the barium salts. If, however, a small first fraction is obtained it will contain all the saturated acids, and the main bulk of the oleic acid will be obtained as the pure middle fraction.

The pure acid so obtained is dimorphous; no reliance can be placed on the melting-point as a criterion of purity. Ultimate analysis is powerless to detect even large amounts of impurity. The purity is best followed by the iodine number. This is the weight of iodine absorbed by 100 grams of the acid. The value for pure oleic acid is 90.07; for the saturated acids it is, of course, zero, while for the acids less saturated than oleic it is correspondingly greater than 90.

The actual value of the iodine number does not mean much alone as mutually-balancing impurities are usually present. A sample of oleic acid can only be called pure if its number is 90, and if this value remains unaltered on further attempts at purification.

The following figures show the progress of the purification of a sample of crude oleic acid by the orthodox<sup>1</sup> lead salt-ether method and by my modified method outlined above; the iodine numbers are the mean of a number of lots.



The small first fraction obtained from the crystallisation of the barium salts of the acid from the lead oxide treatment having an iodine number of 87 was put through the lead oxide treatment again. The iodine number was thereby raised to 90.0, while that of the ether insoluble fraction was 48.5. The saturated impurity so removed proved to be mainly palmitic acid.

<sup>1</sup> Lewkowitsch, *Chemical Technology of Oils, Fats, and Waxes*, 1, 549.

## APPENDIX II

### *The Colour and Thickness of Soap Films*

<i>First Order.</i>	$\mu\mu.$	<i>Fourth Order.</i>	$\mu\mu.$
Black . . . . .	$\left\{ \begin{array}{l} 6 \\ 12 \end{array} \right.$	Grass green . . . . .	597
Silvery white . . . . .	..	Green . . . . .	634
Amber . . . . .	..	Yellow green . . . . .	682
Magenta . . . . .	201	Carmine . . . . .	746
<i>Second Order.</i>		<i>Fifth Order.</i>	
Violet . . . . .	216	Green . . . . .	790
Blue . . . . .	250	Green . . . . .	842
Green . . . . .	290	Pink . . . . .	893
Yellow . . . . .	322	Pink . . . . .	945
Orange . . . . .	348	<i>Sixth Order.</i>	
Crimson . . . . .	371	Green . . . . .	1000
<i>Third Order.</i>		Green . . . . .	1044
Purple . . . . .	396	Pink . . . . .	1100
Blue . . . . .	410	Pink . . . . .	1150
Blue . . . . .	428	<i>Seventh Order.</i>	
Emerald green . . . . .	466	Green . . . . .	1210
Yellow green . . . . .	502	Green . . . . .	1265
Carmine . . . . .	542	Pink . . . . .	1315
Bluish red . . . . .	578	Pink . . . . .	1370
		<i>Eighth Order.</i>	
		Green . . . . .	1420
		Pink . . . . .	1500

This table is calculated from the experimental determinations of the thicknesses made by Reinold and Rücker;<sup>1</sup> it can be seen that they agree with the values calculated from the theory outlined on page 41.

### *Correction for Oblique Observation*

The following table gives the factor by which the apparent thickness of a film calculated from its colour, viewed at an angle  $\alpha$ , must be multiplied to give the true value. The table given by Professor Boys in the second edition of his book needs correction; for the refractive index of soap solution is assumed to be

<sup>1</sup> *Phil. Trans.*, **172**, 456 [1881].

the same as that of water, whereas it is distinctly higher. For all soap solutions in common use the value is 1.41.  $\alpha$  is the angle at which the film is viewed,  $i$  and  $r$  have their usual significance, while the fourth column gives the factor which is, of course, cosine  $r$  in the equation  $\mu\theta \cos r = \frac{n\lambda}{4}$ .

$\alpha$ .	$i$ .	$r$ .	$\cos r$ .
0°	90°	45° 4'	0.706
10°	80°	44° 20'	0.715
20°	70°	42°	0.743
30°	60°	37° 53'	0.789
40°	50°	32° 50'	0.840
50°	40°	27° 12'	0.889
60°	30°	20° 11'	0.939
70°	20°	14°	0.970
80°	10°	7° 7'	0.992
90°	0°	0°	1.000

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